JOURNAL OF APPLIED PHYSICS

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Modern Masterpieces

POPULAR scientific magazines have been giving considerable attention to Professor Ernest O. Lawrence's proposed 2000-ton cyclotron. This project is a most worthy one, and there is little doubt that the money to build it will soon be forthcoming. There seems always to be money available for well-considered and well-thought-out plans, no matter how large an investment is needed.

Physicists and others are likely to become discouraged when the lack of funds makes it necessary to postpone some plan or experiment. Yet we have example after example of magnificent support for those projects which are full of vision and for which the courage exists to see them through. That first great experimentalist, Leonardo da Vinci, had troubles in the fifteenth century just as the rest of us do today. He drew up countless preliminary plans for all manner of projects. Only a few of them were worked out in sufficient detail to gain the confidence of his patron. For those particular projects, however, he drew plans over and over, even for the most minute details. Out of such plans and his persistence have come some of the world's greatest masterpieces.

Support for the 200-inch Mount Palomar telescope didn't come easily. George Ellery Hale had a vision, but he also had detailed plans. He spent many years talking about his plans before the money actually became available. Undoubtedly he became discouraged, but his faith in his vision never lagged. As a result, one of the great masterpieces of the present age is nearly finished. The 2000-ton cyclotron will be a fitting companion piece. There is room and need for more masterpieces of this kind.

These great projects give evidence that there is no lack of money for worthy enterprises. There is rather a lack of ideas, of detailed plans and of the courage to carry the plans through. No project, big or small, is impossible if it is well thought-out. Longfellow realized this full well when he wrote the inspiring stanza which begins, "Let us, then, be up and doing."

Special Issue on Photography

Photography is becoming an increasingly more important branch of applied physics. With the assistance of Dr. L. A. Jones, a special group of up-to-the-minute papers in this field are presented in this issue. They cover the physical basis of image formation, the effect of atomic particles on photographic emulsions and the two most lively issues of the day, color photography and wide aperture lenses. Our sincere thanks go to Dr. Jones.

For February

Stresses in Freely Falling Chimneys and Columns, by FRANCIS P. BUNDY

Electrical Conductivity of Metals, by JOHN BARDEEN

Ferromagnetic Domains and the Magnetization Curve by WILLIAM F. BROWN, JR.

Also contributed original research.

Physics in 1939

THOMAS H. OSGOOD
University of Toledo, Toledo, Ohio

I

DURING the decade which is just closing, three new fundamental particles, the neutron, the positron and the meson have been discovered. In addition, theoretical considerations seem to demand the existence of two others, the neutrino and the neutretto, although decisive experimental confirmation is still lacking. In these few years the inventory of particles has more than doubled. Since much of our present knowledge of all primary particles has been acquired with much ingenuity, in the best manner of detective fiction, by the sifting of conflicting evidence obtained from a study of fog-trails, we celebrate the occasion by printing in Fig. 1 a representative collection from the Rogues Gallery of the Cloud Chamber. Three of these items are shown completely masked, although in appropriate company (such as a hydrogen-containing substance) one of these, the neutron, will betray its passage by producing recoil nuclei.

II

Pride of place among new phenomena in the field of atomic physics must this year be given to the discovery of the fission of the heavy nuclei, uranium, protoactinium, and thorium, which occurs when they are bombarded with neutrons. It would hardly be true to say that the discovery was quite unexpected, for although the effects of neutrons on nearly all the elements in the periodic table were investigated in an exploratory manner several years ago, yet the details of individual processes were far from being accurately known. One of the commonest processes which takes place when a neutron, especially a slow neutron, interacts with a nucleus, is the temporary addition of the neutron to the nucleus, and the emission of radiation. The new nucleus is unstable. A typical example is summarized in the equation

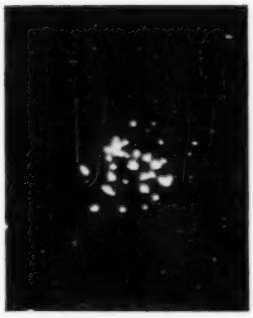
$$Ag^{109}+n^{1}\rightarrow Ag^{110}+\gamma.$$

The synthetic nucleus of mass 110 and charge 47 units still has the chemical properties of silver. But it is unstable, and decays rapidly in accordance with the scheme

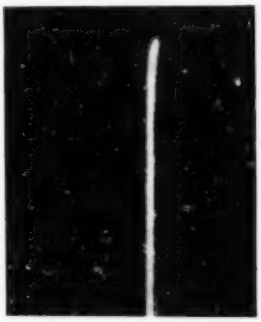
$$Ag^{110}\rightarrow Cd^{110}+e^{-}.$$

The emission of a negative electron increases the positive nuclear charge by one unit, without appreciably diminishing the mass, so that the final nuclear product must have the chemical properties of element number 48, that is, cadmium, with a mass 110. If, however, as happens in other reactions, an alpha-particle, or a proton, or a neutron were emitted in place of, or accompanying the gamma-ray of the first equation, then the final product would, of course, belong to a different atomic species, lower in the periodic table. So well-established were processes of this type that it was practically taken for granted that the interaction of neutrons with nuclei, followed *only* by the emission of beta-particles, would transmute those nuclei into other species one unit higher in the atomic series.

Several years ago during their survey of the effects of neutrons, Fermi and his colleagues bombarded uranium and observed the subsequent emission of beta-rays. It was natural to conclude that the uranium had been transformed into an element of atomic number 93. Thus were born the "transuranic" elements. It happened that the beta-rays emitted during the formation of this and other "transuranic" elements were divisible into many classes, each characterized by its own decay constant. Unfortunately the half-lives were all so short that conclusive evidence as to the nature of the products, such as only chemical separation could give, was well nigh impossible to obtain. Then in 1937 Curie and Savitch discovered a product of period 3.5 hours, and proceeded forthwith to separate it by chemical means. It turned out to be a substance with the chemical properties of lanthanum, although its mode of production entitled it to be classed as a transuranic element. This was the beginning of the end of these mythical elements,



Recoil Nucleus



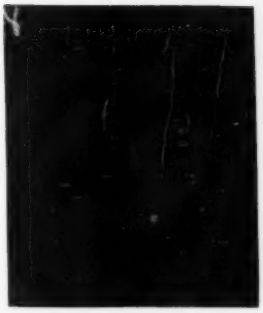
Alpha-Particle

Proton

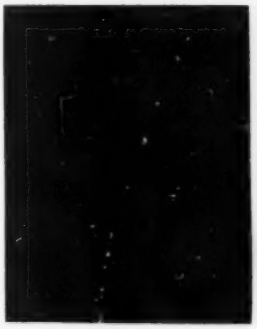
(apart from the 23-minute U^{239}) for soon other products were discovered which had the chemical properties of barium.

Early in 1939, Meitner and Frisch[1] pointed out that most of the inconsistencies among the observations dealing with the nuclear reactions of uranium could be eliminated by supposing that the nucleus formed after capture of a neutron split into two parts of comparable masses. In arguing their case they placed great reliance on the liquid-drop model of the nucleus developed by Bohr, and we quote their own words on this point. "On account of their close packing and strong energy exchange, the particles in a heavy nucleus would be expected to move in a collective way which has some resemblance to the movement of a liquid drop. If the movement is made sufficiently violent by adding energy, such a drop may divide itself into two smaller drops."

"In the discussion of the energies involved in the deformation of nuclei, the concept of surface tension of nuclear matter has been used and its value has been estimated from simple considerations regarding nuclear forces. It must be remembered, however, that the surface tension of a charged droplet is diminished by its charge, and a rough estimate shows that the surface tension of nuclei, decreasing with increasing nuclear charge, may become zero for atomic numbers of the order of 100." Meitner and Frisch predicted that the total kinetic energy of the two receding fragments from the uranium reaction should be about 200 Mev. They remarked also that under neutron bombardment, thorium was already



Neutrino



Positron

Electron

Neutron

Meson

Neutretto

FIG. 1. The Rogues Gallery of the Cloud Chamber. The meson track, noticeably heavier than the electron track in the same picture, is by E. J. Williams, University College, Aberystwyth, and is reproduced from Nature **141**, 684 (1938). The other tracks are from the collection of H. R. Crane, University of Michigan. The range of the recoil nucleus is so small that its track appears merely as a spherical cluster of droplets. The droplets which it has formed here have actually condensed on neutral molecules. Had the ions not been removed beforehand, the droplets would have been far more numerous.

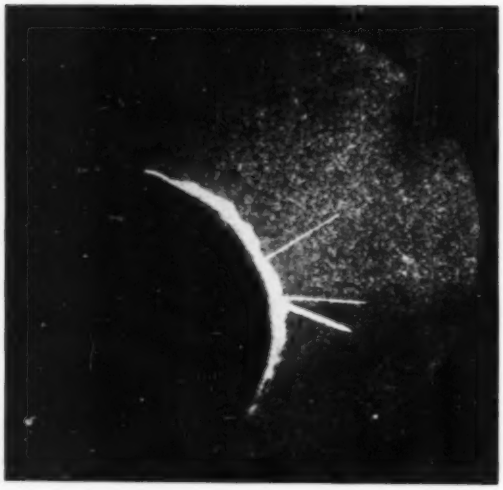


FIG. 2. Fission of uranium. The uranium oxide is deposited on a semi-circular strip backed by a section of paraffin. Fast neutrons are slowed down by the paraffin and bombard the uranium. Two thin tracks due to natural alpha-particles of range about 2.4 cm from U I are seen, and in addition a very heavy track of somewhat smaller range is seen resulting from a uranium fission fragment. The range here is a little more than 2 cm. It happens that there are no alphas from the U II isotope. These have a longer range, about 2.75 cm, and are present in equal abundance. (Photograph by G. L. Weil, Columbia University.)

known to give rise to products, some of whose decay periods were apparently the same as those of the products resulting from the fission of uranium. It was reasonable, then, to suppose that the thorium reaction was a fission process like that of uranium.

It was not long before unambiguous confirmation of these suggestions came from several other laboratories, and we are privileged to reproduce here (Fig. 2) a cloud-chamber photograph made recently at Columbia University which shows the intense ionization along the track of one of the fission products of uranium. As an indication of the interest which this new phenomenon has aroused we may point out that about twenty percent of the Letters to the Editor in the *Physical Review* since February have been concerned with it. To follow these in historical order would probably be confusing, so we shall attempt to give a brief account of the details of the process as they are now known.

Since the masses of atoms in the atomic sequence increase in general faster than twice the nuclear charge, a very heavy nucleus, if split, will divide into two fragments which include more neutrons in proportion to protons than are found in normal atoms of about the same masses as the two fragments. For example, if uranium were to divide so that one immediate product were $_{56}Ba^{139}$, the equation

$$_{92}U^{239} + {}_{0}n^{1} \rightarrow {}_{56}Ba^{139} + {}_{36}Kr^{100} + \text{K.E.}$$

shows that the other fragment (if there be only two) must be krypton, and a very peculiar krypton, with mass 100. This equation must be construed merely as indicating the *kind* of process involved in fission, because chemical analyses show the presence of nearly a dozen elements, solid and gaseous, among the products. These may be in a variety of high energy states. After the splitting of uranium, the question naturally arises as to the ultimate fate of these excess neutrons. Some at least, might be expected to be emitted during the fission process, others might be given out later, as the radioactive fragments decay. Experiments designed to count approximately the numbers of neutrons emitted have been made by Szilard and Zinn,[2] who find that about two neutrons per fission are given out "instantaneously." In addition there is a delayed emission of neutrons[3] with periods of about 12 seconds and 45 seconds. The emission of these neutrons indicates that the first products of fission are probably nuclei in high energy states, and that these decay, some with the emission of neutrons, to more stable forms which are in many cases still radioactive.

As a result of their own experiments Heyn, Aten and Bakker[4] suggest the following sequence for the gaseous products after fission has occurred:

$$Xe^{139} \xrightarrow[0.5\text{ min.}]{} Cs^{139} \xrightarrow[10\text{ min.}]{} Ba^{139} \xrightarrow[87\text{ min.}]{} La^{139} \quad \text{(stable)}$$

$$Xe \xrightarrow[0.5\text{ min.}]{} Cs \xrightarrow[30\text{ min.}]{} Ba \xrightarrow[\text{long}]{} La$$

$$Kr^{88} \xrightarrow[17\text{ min.}]{} Rb^{88} \xrightarrow{} Sr^{88} \quad \text{(stable)}.$$

This evidence supports the idea that the primary process of fission may occur in more than one way; that is, the xenons in the table above are at least in different states of excitation and may well have different masses. Later experiments[5] from

this side of the Atlantic will probably cause a revision of some of the decay periods just quoted.

Neutrons, slow or fast, are able to initiate the uranium-splitting reaction, and during its subsequent course more neutrons are emitted with energies apparently in the range which is effective in causing the primary fission. It is an interesting game therefore, to speculate upon the possibility of a chain reaction[6] going on in a mass of uranium, which might continue with explosive violence once it has been started. Explosive, indeed, would be a mild word to use, for the reaction is, mass for mass, perhaps ten million times as energetic as the explosion of hydrogon and oxygen to form water. To date, there seems to have been no report of such an occurrence. Why not, if two neutrons are given out for every original uranium nucleus which divides? The explanation depends on the effective cross sections of the atoms for the different processes which may occur. If slow neutrons are used to cleave uranium, it turns out that they are also able to transform the U^{238} to U^{239} by radiative capture, and since the latter reaction is very probable, that is, characterized by a comparatively large cross section, it would become operative and quickly use up the slow neutrons which accompany the original breaking down of uranium. On the other hand, if fast neutrons are used to cleave uranium, the other fast neutrons which are emitted during the subsequent reactions have a much greater chance of being scattered (i.e. the uranium atoms have a larger scattering cross section than cross section for fission) than of initiating a new fission process. Hence there is no possibility here of a chain reaction unless many more than two additional neutrons are liberated as a result of the step-by-step decay of the fragments of the primary uranium nucleus. If there actually turns out to be a danger of such a cumulative process in large masses of uranium, it could be prevented by mixing uranium with hydrogen-containing substances. Then, the fast secondary neutrons would very quickly be slowed down so that they could not initiate the fast neutron splitting of uranium, and more slow neutrons would be available for the harmless process of creating the unstable isotope U^{239}. At the present time, the general opinion seems to be that no dangerous chain reaction can occur unless there is an extraordinarily high concentration of the rare isotope U^{235}. And it is comforting to think that during the accumulation of such a single isotope, an explosion would probably occur spontaneously (that is, be initiated by cosmic rays) before the quantity collected reached lethal proportions.

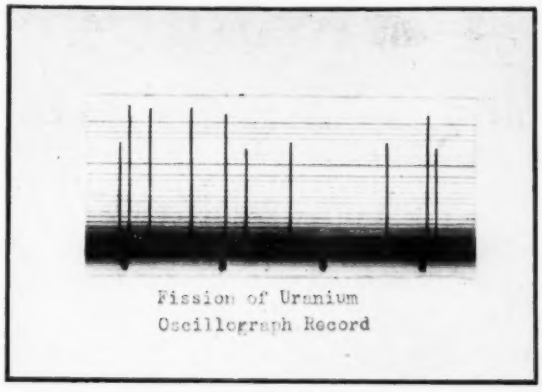


FIG. 3. The ionization caused by the fission fragments was measured in a parallel plate ion chamber, 6 mm deep, containing argon at 100 lb./in.^{2}. The two major groups of fragments stand out clearly, one having about 100 Mev maximum energy, the other about 75 Mev. The alpha-particles cause so insignificant an ionization that they do not stand out from the background. (Courtesy of J. R. Dunning, Columbia University.)

The enigmatic behavior of this U^{239} is an important problem at the moment. It is definitely formed by the resonance capture of neutrons of about 25 electron-volt energy, and thereafter it emits beta-particles with a period of 23 minutes. A true transuranic element of atomic number 93 therefore seems to be formed. But here the clues end. No one has ever detected the emission of alpha-particles from it, nor is any member known of the permanent radioactive family which it would be expected to sire. When Segrè states[7] that "transuranic elements have not yet been observed," his sentence must be interpreted as meaning that the apparent formation of a transuranic element of number 93 must not be taken as final proof that it exists.

Already some aspects of this new disintegration process have been investigated in some detail. For example, Booth, Dunning and Slack[8] have shown that the fragments fall into two distinct energy groups, as illustrated in the oscillograph record in Fig. 3, where each of the long black

vertical lines represents the ionization due to one fragment. This was done by absorbing individual recoiling particles completely in an ionization chamber and measuring the ionization produced. The groups had maximum energies of about 75 and 100 Mev, from which the authors calculate that the ratio of the masses of the two fragments would be about 96/140. This ratio is in good agreement with the chemical evidence which (for Sr/La) would be about 90/140. However, the total energy measured falls short of that predicted by Meitner and Frisch by some 25 Mev, which may well be taken up by secondary processes such as excitation of the nuclear fragments, or else the true energy of recoil may be greater than that which is measured on account of the difficulty of collecting all the ions from tracks of such great ionization density as these heavy nuclei form. The ranges of the particles are quoted by Booth, Dunning, and Slack[9] as 1.5 cm and 2.2 cm, measured in air. It would be wrong to make the assumption that these two groups are homogeneous, that is, that uranium always divides into exactly the same two parts, for Ba, Xe, Kr, I, Te, La, and other elements have been identified among the products of disintegration; yet some authorities seem to think that the primary fission process is comparatively simple,[10] and that the apparent complexity of the products is brought about by their subsequent behavior.

III

Studies of the artificial disintegration of elements are continued with unflagging zeal. New reactions are catalogued, new unstable nuclei are detected, energy levels of nuclei are mapped, new isotopes are discovered. Rather than present a mere condensed catalog of such findings, we prefer to deal with one topic in which the present knowledge of nuclear reactions has been applied to solve the problem of stellar energy. It must come as a keen pleasure to all who have worked during the last decade in the field of nuclear disintegration, to find so direct an application of their researches as this. The information which we now have concerning the conditions which exist in the interior of a star form an outstanding example of deductive logic, for no direct observation can be made at all. The solution of the problem of the origin of stellar energy is restricted at the outset by several well-tested generalizations which have been found from astrophysical observations, and by theories which are based upon them. Any acceptable solution must account for the evolution of a star according to the scheme of the Russell-Herzsprung diagram; it must account for Eddington's mass-luminosity relation; it should show why some stars follow the main sequence, and some are giants; it should offer some plausible reason for the occurrence of white dwarfs; it should be consistent with the known abundance of the different chemical elements in stars; and should explain why stars have their masses grouped in so small a range. While it is too much to hope for a thoroughly satisfactory theory at first, considerable progress has been reported in papers by Bethe,[11] and by Gamow and Teller.[12]

Normally we think of nuclear reactions as occurring when a fast-flying particle interacts with a nucleus. The terrestrial difficulty of accelerating particles to the requisite speeds is absent in the interior of stars, where the thermal velocities (due to a "temperature" of the order of ten million degrees C) are great enough for the purpose. Bethe shows that "the most important source of energy in ordinary stars is the reactions of carbon and nitrogen with protons." In essence these reactions amount to the creation of helium out of protons according to the following scheme:

$$\begin{aligned} &C^{12}+H^1 \rightarrow N^{13}+\gamma \rightarrow C^{13}+e^+ +\gamma, \\ &C^{13}+H^1 \qquad\quad \rightarrow N^{14}+\gamma, \\ &N^{14}+H^1 \rightarrow O^{15}+\gamma \rightarrow N^{15}+e^+ +\gamma, \\ &N^{15}+H^1 \qquad\quad \rightarrow C^{12}+He^4. \end{aligned}$$

The sums of the first and last columns lead to a condensed summary of the reactions, in the form

$$4H^1 \rightarrow He^4+2e^+ +3\gamma,$$

which shows that the process is essentially one of building helium out of hydrogen. For each intermediate atom, C^{12}, C^{13}, N^{14}, N^{15} which is transmuted, another identical one appears later, so that the stock of atoms of these elements remains constant. This cycle, according to Bethe, is the chief one in hot stars. In cool stars a straightforward building up of protons into deuterons, and then further into helium, appears

to predominate, and in average stars, like the sun, the two types of helium building are equally likely. One of the essential points of the theory is the exclusion of reactions involving protons with atoms either heavier or lighter than carbon and nitrogen. Such reactions, of course, could provide the requisite energy, but at the expense of a degradation of the atoms downwards in the periodic table, so that the proportions of most elements would suffer tremendous changes as the star proceeded on its evolutionary course. Since, in all cases, helium is being formed at the expense of hydrogen, it is to be expected that old stars contain a much smaller percentage of hydrogen than young ones. This is well borne out by spectroscopic observations.

Bethe finds that central temperatures of typical stars throughout the main sequence, calculated according to his theory, agree within a few percent with those derived from Eddington's theory which employs observational data to arrive at these temperatures. There is, however, a glaring discrepancy if Bethe's theory is applied to giant stars, so that it must be inferred that some other process is operative in them. Gamow suggests that gravitational condensation, long toyed with as a general source of stellar energy before much was known about the transmutation of elements, is mainly responsible for the energy production in these very diffuse giants.

IV

There is no evidence yet for the failure of the law of conservation of energy or of the law of conservation of momentum in atomic collisions or explosions. These are always assumed to be valid, and if an apparent violation occurs, it is deemed to be due to some cause yet undetected. During the last year or two, Crane and Halpern[13] at the University of Michigan have been measuring carefully the energies and momenta of the particles observed in the β-disintegration of radioactive chlorine (Cl^{38}). If the particles observed, the nucleus and the beta-particle, were the only ones involved, then the momentum acquired by the recoiling atom should be the same as that carried away by the smaller particle. Theoretical treatment of the problem requires the presence of a third particle, a neutrino, in order that energy and angular momentum be conserved, but there are two current variations of the theory, one due to Ferni, the other to Konopinski and Uhlenbeck. They differ principally as to the relative direction of ejection of the neutrino and electron, and as to the proportions of low energy electrons which they predict, the Fermi theory giving more than are found by experiment. It is to be remembered that beta-rays of low energy are much more likely to be missed[14] for reasons including scattering and absorption in a solid source, so that although the Konopinski-Uhlenbeck version seemed to agree closely with experimental results a few years ago, the correctness of that version could hardly be accepted without qualification. Crane and Halpern now find from their cloud-chamber experiments that the momentum of the recoiling argon nucleus (from Cl^{38}) is often much greater than the momentum of the beta-particle. It seems very likely that the neutrino should be burdened with the difference. The next step, of course, would be to discover if possible from the momentum relations in what direction the neutrino escapes with respect to one of the observed momenta. The two investigators tried to do this, but "found that if the results indicate anything at all in this respect, they favor slightly the predictions of the Fermi theory."

V

The literature on cosmic rays is so confusing that it is impossible at the present time to pick out those experiments which will, in later years, prove to be most significant; but before attempting to summarize the conflicting interpretations which have been placed on them, we shall first describe a new multiple counter which represents the latest type of electrical detecting apparatus. This new multiple counter has been developed by Swann and his associates for the study of shower phenomena produced by the penetrating component. The recording devices are housed in the lowest 12-foot section of a vertical cylinder (Fig. 4) whose upper part is filled with water. Beneath this water absorber is a set of six or more tube-counter trays (Fig. 5) each containing 18 units. Every one of these is connected electrically to its own electroscope (Fig. 6) which is provided with a mirror whose movement records

FIG. 4. Tank in which the apparatus is installed. The upper part is filled with water. The counters are in the lowest 12-ft. section. (Courtesy of W. F. G. Swann, Bartol Research Foundation.)

the passage of an ionizing particle through the counter. Above the complete unit is a block of lead 18 cm thick to make sure that the counters record only phenomena associated with the penetrating rays. Furthermore, no electroscope will react unless at least one ray passes through all of the trays of counters. If now a shower is produced in the upper lead block, the flying particles will trip only the counters through which they pass, and the actual paths of these particles are recorded, via the electroscope mirrors, on a photographic plate. The apparatus has been used to investigate the relative numbers of multiple events accompanying the passage of one penetrating ray. As might be expected, the proportion falls off fast as the multiplicity of the events increases. For example, for every twelve events in which a single secondary particle is created, there are only two in which three secondary particles occur. This is in rough agreement with Bhabha's theory of the secondary effects of mesons.

While the soft component of cosmic rays is fairly satisfactorily explained as consisting of electrons produced in showers, the progress of this year's research concerning the penetrating component seems merely to have increased the uncertainty regarding its source, and its behavior is interacting with matter. For a time, however, there appeared to be a hope that some of the phenomena associated with the hard component would become much more simply understandable on the assumption that this hard component consists of heavy electrons or mesons. But this early promise has not been fulfilled. In the first place it has been known for some time that the apparent mass absorption of penetrating cosmic rays is greater in air than in dense materials. This curious fact receives a simple explanation if the meson, which is without question an unstable particle, disintegrates and loses its identity in a mean time of about 2×10^{-6} sec.

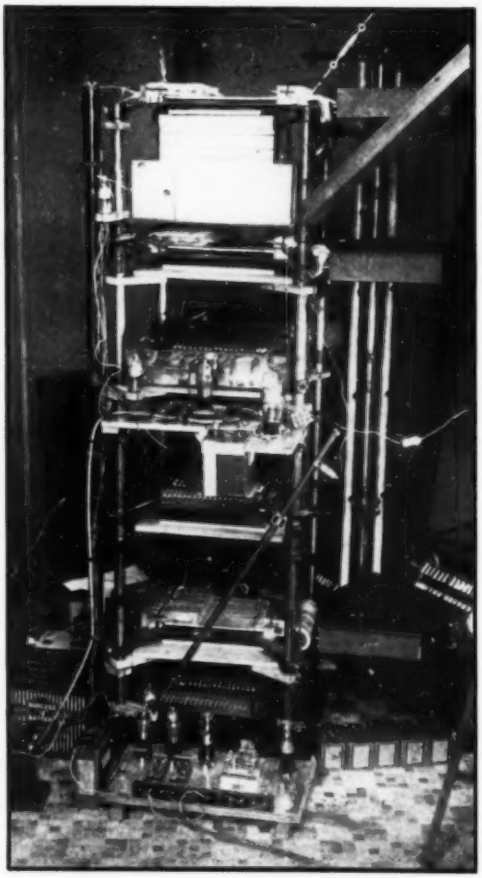


FIG. 5. Assembly of six counter trays. Slabs of lead are seen at the top. (Courtesy of W. F. G. Swann, Bartol Research Foundation.)

after it is born. Usually it is assumed that the meson disintegrates into a negative electron and a neutrino, though recently Majumdar and Kothari[17] suggest that its products may be a neutron and a proton.* It is clear that the time

* This would account readily for the presence of heavy particles which have been found in cosmic rays, but would require that the meson have an initial energy which is at

required by a fast moving particle to traverse (say) 10 cm of lead must be very much less than the time the same particle would take to travel through an equivalent barrier of the atmosphere. 10 cm of lead are equivalent to something of the order of 3 km of air of the lower atmosphere. It would take a particle, even one moving at practically the speed of light, about 1.7×10^{-6} sec. to travel this distance, so that a meson has a good chance of decaying during this time, while the probability would be much greater than it would emerge intact from the 10 cm of lead. Hence the apparent absorption in air must be greater than in a substance such as lead (or even water) for the simple reason that in the atmosphere many of the original mesons disappear on the way to the recording device.

An argument of the same kind shows why the absorption of penetrating cosmic rays in a vertical direction is less than that of rays which have come in obliquely; the particles which come in obliquely have traveled for a longer time, and fewer of them are left. On the assumption that mesons are produced by primary cosmic rays after the latter have traveled one-tenth of the way through the atmosphere from the top (i.e., at 16 km height, where the barometer reads 7.5 cm of mercury), Blackett[18] calculates, with the aid of some meteorological data, that the mean range of mesons before decay is about 25 km. This calculation applies to mesons of the energy group which are likely to die at about sea level. For more energetic mesons, such as can penetrate 60 meters of water, the mean range is much larger. Blackett also suggests that the seasonal variation in cosmic-ray intensity may be due to this characteristic behavior of mesons: in winter the atmosphere is colder, and therefore less thick than in summer (for an equivalent atmospheric pressure). The mesons would therefore traverse it in less time before decaying, with the result that more mesons should reach sea level in winter than in summer, and cause greater currents in ionization chambers there.

Several routes which involve assuming the mass to be about 150 electron masses are available for calculating the decay times of these particles. Blackett gives 1.7×10^{-6} sec., Rossi[19] about 2×10^{-6} sec., and other determinations run a little higher. Nevertheless Nordheim[20] is of the opinion that the strict application of Fermi's theory of β-decay would lead to a theoretical lifetime of the meson some 10^3 times smaller than the observed values just quoted. His suggestion is that the theory requires reformulation, or else

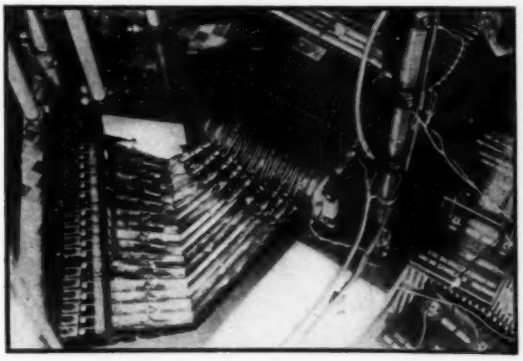


FIG. 6. A tray of counters. The horseshoe-shaped elements to the left indicate the positions of the electroscopes. The transformer and rectifier elements are seen in the center of the picture, leading to a row of 18 counters shown by the cylindrical tubes immediately above the center. (Courtesy of W. F. G. Swann, Bartol Research Foundation.)

that the differences in conditions (e.g. whether the meson is in a nucleus or free) may affect its disintegration in a way which has not yet been taken into account. In this connection Yukawa and Sakata[21] point out that theoretical considerations lead them to believe that the lifetime of the meson would be much longer if its mass were slightly smaller, and that satisfactory agreement with cosmic-ray observations can be obtained only if the mass is taken somewhat lower than the 170-or-so electron masses which cloud-chamber observations suggest. It is interesting to couple this with the theoretical possibility[22] that mesons may occur with masses which vary by perhaps 30 percent. Furthermore, investigations carried out by the Bartol Research Foundation of the Franklin Institute[23] do not seem to be capable of direct interpretation on the basis of the known behavior of mesons as outlined above, and to take care of this difficulty several possible modifications of current ideas are suggested. For instance, the work just quoted could be reasonably understood if there happen to be two types of mesons, a light variety associated directly with

least equal to the sum of the rest mass energies of these two massive particles.

incoming cosmic rays, the other heavier, arising from nuclear disintegration. If this be so, then the mesons whose masses have been determined with some certainty from cloud-chamber photographs must be nuclear mesons, detectable because they have much smaller energies than their lighter brethren which fly with cosmic rays. If, however, the particles are of only one type, the experiments are explicable on the supposition that low energy mesons are so strongly absorbed by nuclei that they never come to rest before losing their identity in a capturing nucleus. Either of these hypotheses would require a drastic modification of the accepted ideas of mesons. They are mentioned here mainly to emphasize the complexity and uncertainty of the present body of knowledge.

A summary of the difficulties and an analysis of possible explanations has very recently been given by Nordheim[21] and by Nordheim and Hebb[25] from whose papers most of the information below is taken. There appears to be no reasonable doubt that mesons are of secondary origin, for if they were originally a component of the primary radiation, practically all of them would decay on their long passage through space on the way to the earth, and there is no process by which the original supply might be re established in the absence of fairly dense matter. Those which are found above ground must therefore be produced in the earth's atmosphere. The outstanding problem at the moment is to determine the nature of the primaries to which mesons owe their brief existence. The possibility that they may be produced by the soft component is a simple but difficult hypothesis, for it predicts, apparently logically, certain details of the process of absorption and creation which are at variance with observations. Nordheim and Hebb are of the opinion that it would not be "impossible to overcome this difficulty by varying the (assumptions as to the) primary distribution, or introducing numerical factors or the like," but they imply that such a solution of the problem would, at present, be unnecessarily artificial; and suggest that the hypothesis of the soft-component origin of the hard radiation be shelved at least temporarily while other possible avenues are explored.

Nordheim then proceeds to discuss the consequences of assuming that protons or neutral particles are the source of mesons. The proton hypothesis is well supported by Johnson's interpretation of his experiments on the east-west effect, but is undermined in an equally telling fashion by other observations on the geomagnetic effect and on the proportion of slow protons found at sea level. With regard to neutral particles as the primaries which might be responsible for the production of mesons, the most likely hypothesis from a theoretical point of view seems to be that the neutrettos or neutral mesons postulated last year by Arley and Heitler play an important rôle. The experimental workers may rebel at this suggestion, on the grounds that the existence of neutrettos has hardly been conclusively demonstrated; and it might be maintained, without undue seriousness, that in the present state of our ignorance it is scarcely possible to deny the presence of any undetected particle as a component of the primary rays, especially as the origin of the rays is still a free field for speculation.

Although to date there appears to be no confirmation of Majumdar and Kothari's[17] suggestion that the meson breaks up into a proton and a neutron, nevertheless there is a growing body of experimental evidence showing that heavy particles in small numbers are found in cosmic rays. For example, Froman and Stearns[26] believe that non-ionizing heavy particles are produced in cosmic-ray showers.

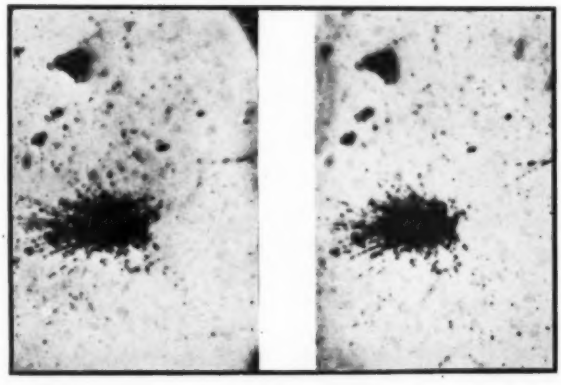


FIG. 7. Stereoscopic pictures of a burst of heavy particles, caused by cosmic rays, in the emulsion of a photographic plate. Magnification about 120 times. Reproduced from Nature **143**, 682 (1939).

They give as evidence the results of experiments of the following type. A triple coincidence

counter system is set up. At the bottom is a pair of counters a little distance apart on the same horizontal level. These are well shielded all round by 10 cm of lead. A little above this lead is the third of the group of counters. A few cm above this is a lead scattering plate. A slab of paraffin is introduced, first between the lead scatterer and the top counter and later between the top counter and the massive lead shielding. Assuming that there are neutrons among the shower particles coming from the lead, it is to be expected that ionizing particles projected by them from the paraffin will trip all three counters, provided, of course, that the paraffin is above the highest counter. The results showed that the ratio of counts per hour with the paraffin above the top counter to the counts per hour with the paraffin below the top counter was about 1.30. With additional support from other like experiments the authors reasoned that non-ionizing particles must occur in showers, and the natural supposition at the present time is that they are neutrons or neutrettos.

Quite recently, Heitler, Powell and Fertel[27] have examined photographic plates exposed (to cosmic rays) both at sea level in England and at a high altitude in Switzerland. They find, of course, that far more long tracks occur at the higher altitude, but by analyzing the results obtained with different amounts of lead round the plates, they conclude that the longest tracks (which are the most significant) are not produced by electrons nor by mesons. There remain neutrons as a probable origin, especially as the tracks have the characteristics[28] of fast moving protons which would be expected to originate in the emulsion.

Spurred by the report of Jesse and Gill[29] that a 30 percent latitude effect is found for very large cosmic-ray bursts, Vallarta[30] speculates upon the occurrence of much heavier particles than those of unit atomic mass. If each burst is caused by one primary particle, then its energy must be so large that if it were an electron or proton its course would be inappreciably affected by the earth's magnetic field. But since there is a geomagnetic latitude effect, these particles must be slower than electrons or protons would be, and to carry the requisite energy they must be fairly heavy. Vallarta suggests that nuclei even as massive as oxygen might behave in a manner which would explain this effect. But he points out that other hypotheses might fit the facts just as well, so that the presence of particles heavier than a neutron remains speculative at present.

Nuclear disintegrations caused by the rays are seldom observed in cloud chambers, but they may be observed much more frequently in thick-emulsioned photographic plates which have been exposed for a long time. A first class example of such an occurrence is given by Jdanoff.[31] His stereoscopic pictures are reproduced in Fig. 7, and show (according to the author) 100 heavy particles originating from a single focus. Electron tracks may also have been present, but are not recorded as the emulsion is not sensitive to them individually. In this burst there are twleve tracks of length equivalent to 18 cm of air, all in roughly the same direction. The total energy liberated must have been of the order of 200 Mev. An interesting feature is the presence of several minor disintegrations within the field of view of the microscope. The frequency of their occurrence, per unit area of the emulsion, turns out to be about seventy times what is normally found, so that there is a strong probability that they represent secondary processes associated with the main large burst. The burst recorded in these pictures is presumably of the same kind as those investigated by Carmichael and Chang-Ning Chou[32] using a thin-walled ionization chamber. They state that the distribution of particles which they find "is due, not to the existence of showers of two kinds, but to the fact (already noted by Auger) that each extensive shower has a core of closely spaced particles surrounded by a relatively wide fringe of much more thinly spaced particles able to produce bursts of small size."

VI

The weigher of atoms is at present content to express his results on a relative scale, taking the mass of the O^{16} isotope to be 16.0000. During the last few years he has been able to attain incredible accuracy in his work, mainly because he is able to measure the mass differences between various atoms in terms of the kinetic energy of disintegration products. This gives him, as it were, an extremely fine adjustment in his weighing, far

exceeding that which can be reached in the absolute measurements such as those which determine the electronic constants. This year notable work has been done at the University of Chicago by Allison and his colleagues. Their experiments are primarily concerned with the determination of the masses of light atoms, and the general method of attacking the problem is well known and need not be reviewed here. One of the key equations which Allison[38] uses is

$$_3Li^6 + _1D^2 \rightarrow 2_2He^4 + 22.08 \pm 0.07 \text{ Mev},$$

in which the letter symbols mean that when a deuteron reacts with a Li^6 nucleus, two alpha-particles are produced. The numerical term means that the two alpha-particles emerge from the reaction with kinetic energy equivalent to 22.08 Mev, or 0.02372 atomic mass unit. These figures, based on a four-year old experiment of Rutherford, Kempton and Oliphant, were believed to be accurate except in the last place. On repeating the experiment with some refinements, however, Smith[34] found that they were too low; his new measurements gave 22.20 Mev in place of 22.08. With this adjustment, the masses of four of the light elements turn out to be

$$Li^6 = 6.01682 \pm 0.00011,$$
$$Li^7 = 7.01814 \pm 0.0009,$$
$$Be^8 = 8.00766 \pm 0.00015,$$
$$Be^9 = 9.01486 \pm 0.00013.$$

It is interesting to compare these and other masses similarly determined with the masses calculated by Barkas[35] on the basis of an empirical-theoretical formula derived from the theory of the nucleus developed in the last two or three years by Wigner and others. It is not possible yet to carry the comparison much beyond atomic number 40, but an inspection of the table which Barkas gives shows a remarkable agreement. It should be noted, however, that on account of uncertainty regarding some of the constants occurring in the theory, the calculated values are not unique, though these constants can be chosen arbitrarily to give good accord with experimental results. Determination of other nuclear masses will therefore be immediately useful in working out further details of the theory.

In 1936 Oliphant pointed out that the mass of Be^8 appeared to be almost exactly twice that of the alpha-particle, with nothing to spare for binding energy, so that it could scarcely be expected to be stable; indeed, Livingston and Bethe's table (1937) quotes its mass as a trifle *more* than that of two alpha-particles, although the difference was easily covered by the uncertainties in the data. Then Skaggs reported that his experiments implied that Be^8 was stable by 0.000174 mass unit, but the latest dispatches throw doubt on this, and leave the question entirely open.

Heavy atoms cannot yet be handled by the methods which are used for the light ones, for a tremendous chain of accurately known nuclear reactions would be required to link each to its predecessors in the periodic table. Masses can, however, be determined by the mass spectrograph by the method of bracketing. Dempster has used this method very successfully to determine the masses of many heavy elements. Usually the masses of the heavy atoms are not quoted directly on the scale $O^{16} = 16.0000$, but are expressed in terms of the packing fraction which is essentially a measure of the relative deviation from the simple whole number rule. With Dempster's instrument, Graves[36] has found the packing fractions for a number of elements in the range of atomic weights between 100 and 200. These substantiate the general trend of the packing fraction curve and confirm the gentler slope which has already been reported in the neighborhood of platinum and gold. When the relative abundances of the various isotopes are taken into account the agreement with recent chemical determinations of atomic weights is very satisfactory.

VII

The tentacles of spectroscopy are so far reaching that we shall be content here to point to three notable landmarks which represent the completion of new work. The first of these is the publication of the *Massachusetts Institute of Technology Wavelength Tables*, compiled under the direction of Professor Harrison. This new book contains over 100,000 entries "giving the wavelength, the intensity in arc, spark, or discharge tube, the stage of ionization of the parent atom when the line has been classified in a term array, and the wavelength authority, for each of the most

important known spectrum lines emitted between 10,000 and 2000 angstroms by atoms in the first two stages of ionization." More than 75,000 of these lines are the results of recent measurements made in the M.I.T. laboratories and have replaced older and less reliable values already in the literature. Such a tremendous undertaking could hardly have been carried through before its results began to be obsolete without a machine which measures the spectrum lines and computes and records their wave-lengths and intensities automatically. An instrument which performs these functions, and which can be attached to a moving plate comparator, was built in the early years of this decade and described[37] in the literature in 1935. A general view of the machine is given in Fig. 8 with Professor Harrison at the controls. It gives a 20-fold increase in speed over the usual manual methods, with an accuracy as great as that which can otherwise be obtained without resorting to interferometer methods of determining the wave-lengths of individual lines.

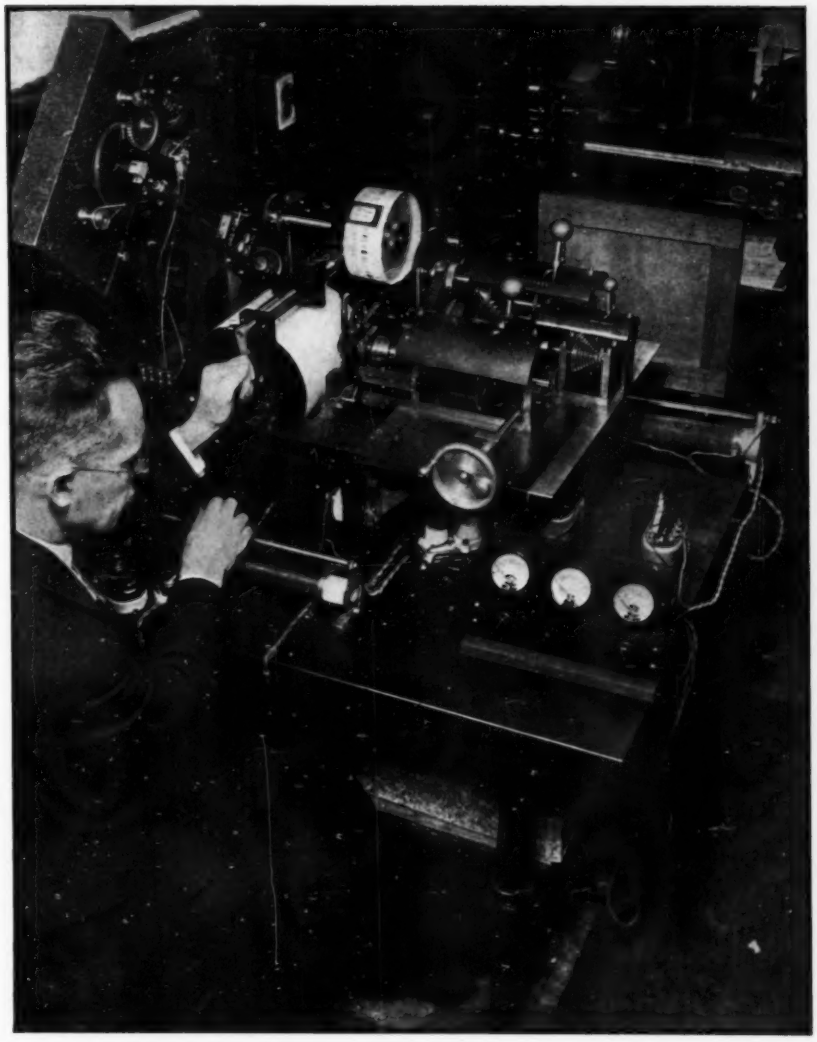


FIG. 8. Machine for measuring and computing wave-lengths of spectrum lines. Professor George R. Harrison is seen operating the machine. (Courtesy of News Service, Massachusetts Institute of Technology.)

As a second example of progress in spectroscopy we reproduce in Fig. 9 rotational spectra of water and of heavy water to illustrate the work which is being carried out under the direction of Professor Randall[38] at the University of Michigan. Of the various types of radiation emitted by a polyatomic molecule, the rotational spectrum involves the smallest energy changes, and therefore lies in the most extreme part of the infra-red, at wave-lengths of the order of 50μ. Such a spectrum can be studied successfully only in absorption, with special echelette gratings in a vacuum spectrograph.[39] The spectra in the figure cover the range 31.6μ to 38.3μ, and are parts of the rotational spectra of H_2O and of D_2O between 30μ and 150μ. An elementary interpretation can be obtained by imagining one of the figures to be cut along its axis of symmetry; then considering the profile of the top half only, it may be regarded as a microphotometer tracing of the absorption spectrum. The symmetry of the records is caused by the nature of the recording and amplifying devices. Dips in the profiles correspond to absorption lines whose positions can be determined with an accuracy of about 0.5 cm^{-1}; and a pair of absorption lines of similar intensity can be detected

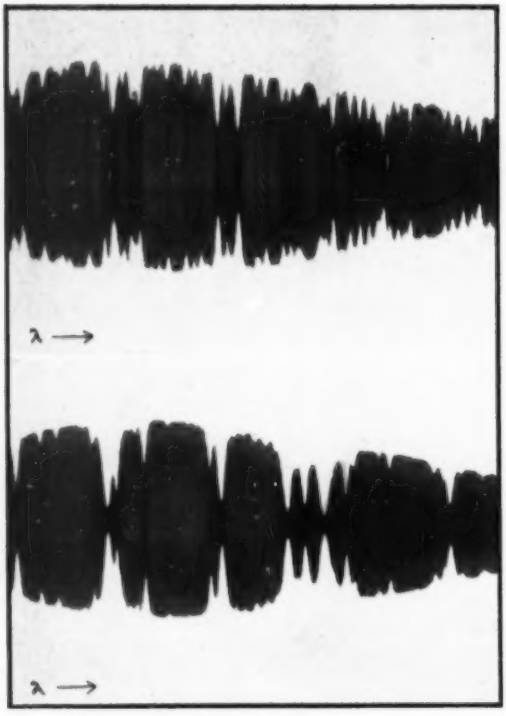


FIG. 9. Photographic reductions of the recordings of the far infra-red spectra of D_2O (above) and H_2O (below) between 31μ and 38μ by a vacuum spectrograph using a grating with 600 lines per inch. The grating has a ruled surface 10×20 inches. The maximum deflection in these records is 290 mm. The records represent parts of the rotational spectra of D_2O and H_2O, obtained by N. Fuson and H. M. Randall at the University of Michigan. The two records differ noticeably in structural detail. (Courtesy of H. M. Randall.)

as double if they are not closer than 0.05 cm^{-1}. The rotation frequencies given by the spectrum of D_2O have been analyzed in terms of energy levels of the molecule, in the fashion used two years ago for H_2O. It is interesting to note that a molecule stretches as it rotates (of course, the stretching will depend on the frequency of rotation) and that corrections can be applied successfully so as to express the energies of the lines in terms of a common standard.

Turning for the third example to atomic spectra we call attention to the work of Jenkins and Segrè[40] on the quadratic Zeeman effect. This is an unsymmetrical splitting and displacement of the lines of an atom by a magnetic field; the effect is small and should be most easily detected for high series members, since it depends on the fourth power of the total quantum number. Large enough values of the quantum number are brought into play only in absorption spectra, which in turn requires a magnetic field of large extent. The authors took advantage of the large field available in the new cyclotron magnet of the Crocker Radiation Laboratory of the University of California, which was available while the vacuum chamber for the cyclotron itself was being constructed. The magnet with spectroscopic equipment in place is shown in Fig. 10. Good spectrograms were obtained showing the effect both in sodium and potassium. The photograph shows, in the background, the hydrogen lamp for producing the continuous spectrum; and, in the left foreground the 3-meter Littrow quartz spectrograph which gave a dispersion of 0.8A per mm in the region used. By the appropriate placing of extra iron, a field of 27,000 oersteds was obtained over a space 5×15×60 cm. This enabled the series lines to be studied up to the total quantum number 30.

VIII

It has been on record in the literature for several decades that the reflection of light from clear glass could be diminished markedly by certain chemical treatments of the surface; but although experiments were done to measure the change in reflectivity there was no appreciation of the reasons for the phenomenon, nor any thorough-going analysis of it. It was known, of course, that the partial extinction of the reflected light was due to some kind of film on the surface, so that when the technique of building up very thin films was developed, as it has been in the last few years, the time was ripe for a systematic study of their action in subduing undesirable reflections. Such a study was published in February by Blodgett,[41] and its most striking features are probably well known on account of the publicity given to it in the daily press. In the first place Blodgett recognized, as Strong had done a few years earlier, that the presence of a thin film on a piece of glass would affect the reflection by a process of interference. Her paper shows that the intensity of light so reflected depends on the refractive index of the glass, the wave-length of the light, and the factors which affect the equivalent optical path of the incident light in the film. The particular case which is

most important from a practical point of view is that in which the light is incident normally. In this case the reflected beam should be extinguished entirely for one particular wave-length, if the refractive index of the film is equal to the square root of the refractive index of the glass, and provided furthermore that the film thickness is an odd multiple of one-eighth of the wave-length. The film must be of unusually low refractive index, therefore, to be most effective. The well-known thin films of barium stearate have a refractive index of the order of that of glass (*ca.* 1.5), but this can be reduced materially by soaking in benzene, which removes the excess of stearic acid, leaving the stearate as a skeleton film of very nearly the same thickness as before. Blodgett chose cadmium arachidate* as the film material, for after a treatment of a similar type it gives a skeleton film of very nearly the correct refractive index. How well the reflection from glass is suppressed may be judged from the accompanying Fig. 11, which was specially prepared for this journal by Dr. Blodgett. Unfortunately these films are sensitive to mechanical and actinic damage, but if protected from such

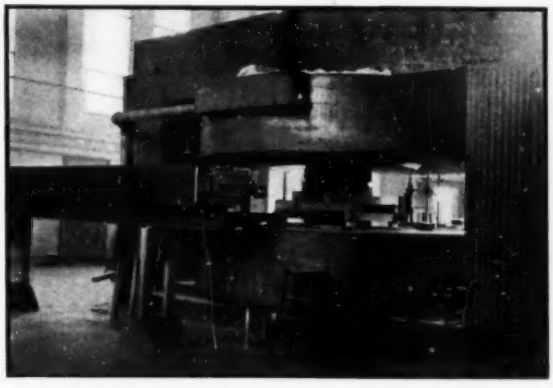


FIG. 10. The new cyclotron magnet of the Crocker Radiation Laboratory of the University of California arranged for studying the quadratic Zeeman effect. (Courtesy of F. A. Jenkins.)

treatments there seems to be no reason why they should not retain approximately the same properties for a long time.

Reflection-destroying films can also be prepared by evaporating in vacuum the right

FIG. 11. One-half of the glass face-cover of this alarm clock has been covered (both sides) with a nonreflecting film. (Courtesy of K. B. Blodgett, Research Laboratory, The General Electric Company.)

amounts of certain substances which have low refractive indices. Several experimenters have used this technique with MgF_2 and other fluorides which are the most readily available substances with about the right indices. These films, like cadmium arachidate films, reduce the reflected light to one percent or less, but no films have yet been made which possess the permanence of the glass surfaces which they cover.

IX

It is little more than six years ago that the magnetic moment of a *nucleus* was first measured by Stern and his colleagues. Before that time, indeed, the magnetic moments of complete *atoms* had been measured, but there the overwhelming contribution is made by the electrons which form part of the normal structure. To measure the nuclear moment it was necessary somehow to get rid of the disturbing electronic contribution, and also to make the measurements more delicate and the dispersion greater. There have been, of course, many calculations of nuclear moments based upon hyperfine structure measurements, but it is desirable to have an experimental method of comparable precision if only to justify the theoretical values.

An important new experimental technique was described in some detail early this year by Rabi,

* Stearic acid, $CH_3(CH_2)_{16}$ COOH; arachidic acid $CH_3(CH_2)_{18}$ COOH.

Millman, Kusch and Zacharias.[42] They show that the principle upon which the method is based is applicable to any system which has angular momentum and magnetic moment. If some details are omitted, the general scheme may be summarized as follows. Molecules are projected first through a magnetic field, inhomogeneous in the two directions at right angles to the general direction of projection. This acts as a selector. Then, a little farther on, they go through another inhomogeneous field whose gradient is opposite to that of the first. This field acts as a kind of analyzer. Regarding an atom as a tiny magnet, it is clear that it will be pushed one way by the first field and back again by the second field. Some typical molecules which start out at a slight angle to the axis of symmetry of the molecular beam will be deflected just the right amount and in the right direction to bring them back to the axis after passing through each field. But between the two inhomogeneous fields is a steady field of smaller extent and also a small oscillating field. Here some of the molecules undergo a process of reorientation if their Larmor precessions are in resonance with the oscillating field; they acquire magnetic properties which distinguish them from their fellows, and prevent them from returning to the axis of the system along with the group with which they started. Hence a fraction of the molecules which would otherwise reach a collector do not. This effect is dependent upon the frequency of the oscillating field, and in principle a measurement of the frequency ν leads to an evaluation of the magnetic moment μ in the equation $\nu = \mu H_0 / Jh$, where J is the angular momentum of the atom and H_0 is the strength of the field in which reorientation occurs.

If a study is to be made of nuclear magnetic moments the most convenient subjects for observation are atoms in a state with electronic angular momentum equal to zero, or molecules in which the electronic angular momentum of one constituent is approximately balanced by that of the other constituents. It happens that the nuclei Li^6, Li^7 and F^{19} can be investigated in the molecules LiCl, LiF, NaF and Li_2. The values turn out to be 0.820, 3.250 and 2.622 in nuclear magnetons. The possible error of these values is given by the authors as about 0.3 percent, and in view of the fact that the values obtained from the best hyperfine structure calculations differ from the experimental ones by about two percent, the question is raised whether the accuracy of the assumptions which go into the theoretical calculations is as great as is generally believed. In later papers by the same workers, many more nuclear magnetic moments have been determined experimentally in the way described above, and in general the evidence seems to point to the trustworthiness of the indirect calculations made on the basis of hyperfine structure measurements.

X

We have had space here to touch on only a few of the recent developments in fundamental physics. The new contributions to applied physics which keep pace with these advances are probably well known to readers of this Journal. Muskat and Morgan[43] have continued their important studies in the lubrication of journal bearings both theoretically and experimentally, generalizing the earlier theory of Sommerfeld to include bearings of length as short as half the bearing perimeter. Another excellent series of papers[44] comes from Stanford University. They deal with klystron oscillators, which are devices for the generation of electromagnetic oscillations at wave-lengths of 10 cm or less. Such oscillations can, of course, be produced by the classical Hertzian methods and by triodes, but in both cases there are great difficulties from the points of view of convenience, stability and efficiency. The new klystron oscillator employs a tube (it really *is* the tube) in which a beam of electrons is sent through a pair of grids between which a small oscillating field is maintained. The emergent beam therefore consists essentially of a fluctuating electron current superimposed upon a direct electron current. When this particular cathode-ray stream is sent through another pair of grids between which is another appropriate alternating field, a considerable fraction of the power originally supplied can be withdrawn in the form of high frequency oscillations. Webster[45] calculates that the maximum attainable efficiency is 58 percent.

These two series of papers on applied physics are worth at least a cursory inspection by the general reader if only for the reason that they

bring out clearly one of the essential differences between pure and applied physics. On the more practical side of the science there is a rapid and harmonious matching of experiment and theory; experiment is usually in the lead, for it often deals with some common detail of modern engineering equipment. On the academic side, as in the study of the fundamental particles, there are theories in abundance, and the most recent developments may take on a speculative aspect, since crucial experiments are frequently beyond the range of present-day technique.

Bibliography

1. L. Meitner and O. R. Frisch, Nature **143**, 239 (1939).
2. L. Szilard and W. H. Zinn, Phys. Rev. **55**, 799 (1939).
3. E. T. Booth, J. R. Dunning and F. G. Slack, Phys. Rev. **55**, 876 (1939).
4. F. A. Heyn, A. H. W. Aten, Jr., C. J. Bakker, Nature **143**, 516 (1939).
5. G. N. Glasoe and J. Steigman, Phys. Rev. **55**, 982 (1939).
6. F. Adler and H. von Halban, Jr., Nature **143**, 793 (1939).
7. E. Segrè, Phys. Rev. **55**, 1104 (1939).
8. E. T. Booth, J. R. Dunning and F. G. Slack, Phys. Rev. **55**, 981 (1939).
9. E. T. Booth, J. R. Dunning and G. N. Glasoe, Phys. Rev. **55**, 892 (1939).
10. N. Feather, Nature **143**, 877 (1939).
11. H. A. Bethe, Phys. Rev. **55**, 434 (1939).
12. G. Gamow and E. Teller, Phys. Rev. **55**, 791 (1939).
13. H. R. Crane and J. Halpern, Phys. Rev. **56**, 232 (1939).
14. See, for instance, J. L. Lawson, Phys. Rev. **56**, 131 (1939).
15. W. F. G. Swann and W. E. Ramsey, Phys. Rev. **55**, 599 (1939).
16. H. J. Bhabha, Proc. Roy. Soc. **164**, 257 (1938).
17. R. C. Majumdar and D. S. Kothari, Nature **143**, 796 (1939).
18. P. M. S. Blackett, Nature **142**, 992 (1938).
19. B. Rossi, Nature **142**, 993 (1938).
20. L. W. Nordheim, Phys. Rev. **55**, 506 (1939).
21. H. Yukawa and S. Sakata, Nature **143**, 761 (1939).
22. P. Weisz, Phys. Rev. **55**, 1266 (1939).
23. C. G. Montgomery, W. E. Ramsey, D. H. Cowie and D. D. Montgomery, Phys. Rev. **56**, 635 (1939).
24. L. W. Nordheim, Phys. Rev. **56**, 502 (1939).
25. L. W. Nordheim and M. H. Hebb, Phys. Rev. **56**, 494 (1939).
26. D. K. Froman and J. C. Stearns, Phys. Rev. **54**, 969 (1938).
27. W. Heitler, C. F. Powell, G. E. F. Fertel, Nature **144**, 283 (1939).
28. Cf. T. R. Wilkins and H. J. St. Helens, Phys. Rev. **54**, 783 (1938).
29. W. P. Jesse and P. S. Gill, Phys. Rev. **55**, 414 (1939).
30. M. S. Vallarta, Phys. Rev. **55**, 583 (1939).
31. A. Jdanoff, Nature **143**, 682 (1939).
32. H. Carmichael and Chang-Ning Chou, Nature **144**, 325 (1939).
33. S. K. Allison, Phys. Rev. **55**, 624 (1939).
34. N. M. Smith, Jr., Phys. Rev. **56**, 548 (1939).
35. W. H. Barkas, Phys. Rev. **55**, 691 (1939).
36. A. C. Graves, Phys. Rev. **55**, 863 (1939).
37. G. R. Harrison, J. Opt. Soc. Am. **25**, 169 (1935).
38. N. Fuson, H. M. Randall and D. M. Dennison, Phys. Rev. **55**, 590 (1939).
39. H. M. Randall, Rev. Mod. Phys. **10**, 72 (1938).
40. F. A. Jenkins and E. Segrè, Phys. Rev. **55**, 52 (1939).
41. Katharine B. Blodgett, Phys. Rev. **55**, 391 (1939).
42. I. I. Rabi, S Millman, P. Kusch and J. R. Zacharias, Phys. Rev. **55**, 526 (1939).
43. M. Muskat and F. Morgan, J. App. Phys. **10**, 398 (1939) and earlier papers.
44. W. W. Hansen, J. App. Phys. **9**, 654 (1938); **10**, 38 (1939). W. W. Hansen and R. D. Richtmyer, J. App. Phys. **10**, 189 (1939). R. H. Varian and S. F. Varian, J. App. Phys. **10**, 321 (1939).
45. D. L. Webster, J. App. Phys. **10**, 501 (1939).

Theory of the Photographic Latent-Image Formation

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THE literature on the subject of the photographic latent image is very extensive. Work on this subject dates back to the beginning of photography now more than one hundred years ago. In the present paper an attempt will not be made to go into all the various theories which have been proposed to account for the latent-image process, but rather the discussion will be devoted mainly to an outline of the important developments during the past twenty-five years which have contributed to the theory of latent-image formation, and to a description of the most recent theories held on the subject.

The photographic emulsion consists of a suspension of tiny crystals of silver halide (usually silver bromide with small percentages of silver iodide) in gelatin.[1] A photomicrograph (2500X) of the grains of a typical emulsion is shown in Fig. 1. In the ordinary multilayer emulsion there are approximately 10^9 grains per square centimeter of plate area, and the average areas of the grains vary from about 0.1×10^{-8} cm^2 for low speed positive emulsions up to 1.0×10^{-8} cm^2 for high speed negative emulsions. The grains consist mainly of flat plates* of triangular and hexagonal forms with some needles. The flat plates, in general, have a thickness about one-tenth their diameter. The structure of the silver bromide crystal is of the regular cubic type and the flat sides of the grains seen in Fig. 1 are the octahedral faces of the cubic structure. These faces are thus of a single ionic type, i.e., Ag^+ or Br^-. When light of the proper wave-length falls on an emulsion, some of the grains (the number depending upon the amount of the exposure) are altered in such a manner that they react differently toward certain reducing agents known as developers. That is to say, those grains which have been affected by the light are reduced to metallic silver by the developer while the other grains are not reduced at all. This developable state produced in a photographic grain by the action of light is called the "latent image."* Although experiments have been carried out with the purpose of detecting the latent image directly, thus far none of these experiments has been decisive and developability still remains the sole criterion for certain detection of the latent image. The fact that the latent image is not susceptible to direct observation is not surprising when consideration is given to the minuteness of the change which takes place in a single photographic grain in a normal exposure to light. From absolute sensitivity measurements,[2] it can be shown that the most sensitive photographic grains are rendered developable by the incidence of a few (one to twenty quanta of light) and therefore only a small number of molecules can be involved. Despite the smallness of the change which takes place in latent-image formation, a photographic grain is nevertheless capable of retaining this altered state for a long time. This is known from the fact that an exposed photographic emulsion can be kept for years[3] before it is developed and still reproduce faithfully the light impression of the original exposure.

Basic Facts

Before entering into a discussion of the theory of latent-image formation, some of the fundamental facts, which are known about the behavior of silver bromide under the action of light, will be reviewed.

It is well known[4] that silver bromide darkens on excessive exposure to light, bromine gas being liberated and metallic silver in the colloidal state being left behind. This decomposition takes place under the action of light absorbed by silver bromide and occurs in the grains of a photographic emulsion as well as in gelatin-free silver bromide. It has been shown[5] through x-ray examination that the first visible traces of an image on silver bromide gives x-ray powder diagrams

* Emulsions prepared in the presence of ammonia tend to have spherical grains.

* While developability of a grain can be produced by other agencies than light, e.g., by pressure, heat, and certain chemicals, we will use the term "latent image" here in the restricted sense as pertaining to light.

identical with those of metallic silver. By these experiments and many others, it has been well established that the action of light in sufficient quantity on silver bromide will give rise to silver and bromine.

According to the Einstein photoequivalence law, each absorbed quantum $h\nu$ should lead to the decomposition of one molecule of silver bromide giving one atom of silver and one atom of bromine. Eggert and Noddack[6] investigated the photochemical equivalence for the direct reduction of silver bromide by light and concluded from their results that this law is approximately fulfilled, the departure from equivalence being within the limit of experimental error of their measurements.

All of the foregoing observations apply to the direct photochemical decomposition of silver bromide in sufficient quantity for direct measurement and thus correspond to exposures far in excess of those required to produce the latent image. The importance of these facts, however, for the present discussion is that radiations of the same wave-lengths which produce the above effects will also produce the latent image. It is therefore natural to suspect that the above effects are in some way a continuation of the processes involved in latent-image formation.

The latent image itself cannot be extracted by chemical reagents in sufficient quantity to be analyzed. Nevertheless a great deal of work has been done on the latent image from the chemical side and the results have been interpreted from the effects upon the developed image. In this way it has been found[7] that the latent image can be destroyed by oxidizing agents such as chromic acid, free halogens, or bodies which readily give up halogen, and by most strong oxidizing agents such as potassium persulfate and potassium permanganate.

The Latent Image Composed of Metallic Silver

From a large mass of evidence of which the above experiments are typical, the theory which has now gained most wide acceptance is that the latent image consists of metallic silver adsorbed to silver bromide. The suggestion that the latent image is composed of metallic silver was made as early as 1839 by Arago[8] in connection with the Daguerre process. The idea was expressed again by Guthrie in 1850. However the silver nucleus theory in its present-day form cannot be said to date from any particular individual. It slowly emerged through the works of a large number of investigators of which the names of Carey Lea,[9] Ostwald,[10] Abegg,[11] and Lüppo-Cramer[12] should be mentioned. Previous to the acceptance of the silver nuclear theory was the alternative theory that the latent image consisted of a sub-halide and it was only with reluctance that this theory was finally abandoned. One of the chief points in favor of the sub-halide theory and at the same time an objection to the silver nucleus theory was the lack of complete parallelism between the destructive action of oxidizing agents on the latent image and on free silver. Lüppo-Cramer pointed out that this objection to the silver nucleus theory could be ruled out by the modified view that the latent image is silver in the adsorbed state and thus less susceptible to chemical attack than free silver would be.

Granting that the latent image consists of metallic silver adsorbed to silver bromide, there remains the question as to the mechanism whereby silver can be formed by the action of light. For information on this question we turn to experimental work which proceeded along somewhat different lines from those already described. It is known[13] from microscopic examination of exposed and developed photographic plates that the individual grains of the emulsion

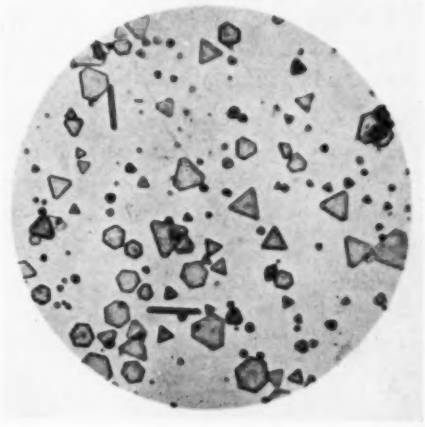

FIG. 1. Photomicrograph (2500X) of the grains of a photographic emulsion.

act as the units in exposure. That is, it had been found that individual grains of an exposed plate either developed entirely or not at all. Accordingly a method which was early invoked as a useful means of study of the photographic problem consisted of microscopic examination of individual grains and the determination of the percentages of these grains made developable with increasing exposures.[13] Some of the most important investigations of the photographic process were carried out in this way, using very thinly coated emulsions in which the grains were in a single grain layer.

Hodgson[14] (1917) was the first to show that the development of an exposed photographic grain begins at a few discrete points on the surface of the grain and proceeds from these points to the entire grain. A photomicrograph showing exposed and partially developed grains is reproduced in Fig. 2.

Svedberg,[15] using single grain layer plates and a specially favorable technique of development, made an extensive study of these points on the grains from which development begins. Svedberg showed that the number of these "reduction centers" on a grain increases with the amount of the exposure given the grain and that the numbers of centers on grains of a single size-class have a distribution in accordance with the laws of chance. That is, if the average number of reduction centers on one grain is $\bar{n}$, then the probability of a grain having n centers is given by the formula

$$P(n)=\frac{\bar{n}^n e^{-\bar{n}}}{n!}.$$

This work indicated that the latent image, instead of being spread uniformly over the surface of a grain, is concentrated in discrete points. From this work by Svedberg and further work along similar lines by Toy,[16] Clark,[17] and workers in the Kodak Research Laboratories,[18] it was established that the formation of the latent image is intimately tied up with certain sensitivity centers which are present on the surface of the grain prior to exposure. If metallic silver constitutes the latent image then it appeared necessary to conclude that the silver is formed preferentially at certain discrete points on the grain.

A great deal of experimentation was carried on in an effort to find out more about the nature of these sensitivity centers which could act to concentrate the action of the light at certain discrete points. An important step forward was made in 1925 by a remarkable work carried out by S. E. Sheppard.[19] It had been known for some time prior to this work that certain gelatins would produce sensitive emulsions, while others would not, even though the gelatin appeared to be similar in other respects. It was natural to attribute these differences to chemical constituents of the gelatin. Working along these lines, Sheppard, by means of a long and laborious series of chemical analyses of the acid deliming liquors obtained through the process of gelatin manufacture, succeeded in isolating the sensitivity-promoting substance of gelatin and in showing that it consists of traces of organic sulfur com-

FIG. 2. Photomicrograph (2500X) of exposed and partially developed photographic grains.

pounds of which allyl isothiocyanate is typical. It was found that the presence of these substances in concentrations of the order of one part in a million is sufficient to render a gelatin active. These materials tend to combine with silver bromide, forming complexes, which in the pres-

ence of alkalis undergo internal decomposition, giving rise to silver sulfide. From these researches it was shown to be very probable that the sensitivity centers on the photographic grain consist of minute specks of silver sulfide, which are formed there during the process of emulsion manufacture. Subsequent work of a chemical nature carried out directly on the photographic emulsion gave supporting evidence that the sensitivity specks did consist of silver sulfide. It was shown that the sensitivity centers are affected by hydrogen peroxide[20] and by sodium arsenite[21] in much the same way as by light, and that they can be destroyed by chromic acid. In further work by Clark,[22] using persulfate solutions of varying potential, evidence was presented to show that the sensitivity centers contain silver in addition to silver sulfide. Subsequent quantitative microchemical determinations in the Kodak Research Laboratories have shown that silver sulfide is largely preponderant, but that much smaller amounts of silver are generally present.

It thus came to be fairly well established that the sensitivity specks on the grains, around which the latent image forms, consist of silver sulfide with perhaps small traces of silver in addition.

The Concentration-Speck Theory

As a result of an exhaustive study of all the experimental work on the subject and after a great deal of experimentation on their own part, Sheppard, Trivelli, and Loveland[23] (1925) announced the *concentration-speck theory* of latent-image formation. According to this theory the light active in latent-image formation is absorbed at random points over the entire surface of the silver bromide grain, but the silver atoms are formed only adjacent to the silver sulfide sensitivity specks. The only function attributed to the speck by this theory is that of concentrating the silver atoms formed during the exposure to light. To account for the fact that light absorbed at random points all over the grain can act to produce silver atoms only at certain discrete points, the idea of transfer of energy by radiationless collisions was introduced. That is, a light quantum incident at a point remote from a speck is supposed to be absorbed by the electron of a Br^- ion and raise its energy state to a higher level. This energy is then assumed to be transferred by radiationless collisions from one atom to another until the edge of a speck is reached. At this point it is supposed that the electron of the Br^- ion is completely released and the photochemical reaction occurs:

$$Br^- + h\nu \rightarrow Br + \text{electron},$$
$$Ag^+ + \text{electron} \rightarrow Ag,$$

the electron transfer from the Br^- ion to the Ag^+ ion giving a neutral atom of silver. Though the mechanism invoked to explain the energy transfer is not entirely satisfactory, nevertheless the *concentration-speck theory* has been recognized from the beginning as an important step in the explanation of the latent-image process. Though later work has modified somewhat the view as to the details of the process whereby the latent-image silver is coagulated around the sensitivity specks, the basic idea of the *concentration-speck theory* has not been overthrown.

At this stage, some important studies were carried out by Toy on the photoconductance properties of silver bromide. It had been known for a long time that silver bromide showed increased conductivity on exposure to light. Toy[24] demonstrated for the first time that the spectral sensitivity of this effect and that of the photographic process agreed in the region of their long wave threshold. On the basis of these findings, Toy proposed that the photoconductance effect in silver bromide constitutes the primary process of latent-image formation.

Of parallel importance to the work on photoconductivity by Toy were the studies carried out about the same time on the photovoltaic effect at Ag : AgBr electrodes by Sheppard and Vanselow.[25] These studies were of complementary character and importance to Toy's work because they demonstrated the simultaneous production of conduction electrons and reactive bromine on absorption of light by silver bromide. Furthermore, these studies established that photoelectrons would transfer directly into contiguous metallic silver without an impressed electromotive force, a fact which will be seen later to have significance in the more recent theories of this subject.

Trivelli[26] (1928) making use of the properties of photoconductance and electrolytic conduc-

tivity of silver bromide, outlined a novel mechanism of latent-image formation based on an electrolytic cell type of action. Fundamental to his theory is the idea that the sensitivity specks consist initially of silver sulfide plus a trace of silver. The silver sulfide is assumed to act as anode, and the silver speck as cathode, of a cell of which the solid silver bromide constitutes the electrolyte. According to the scheme proposed, on exposure to light, electrons pass from the silver sulfide through the silver bromide to the silver while silver cations of the silver bromide pass from the silver bromide to the silver cathode. Thus the silver speck originally present is assumed to grow by electrolytic deposition of silver until it reaches a developable size. Certain features of this cell action are not entirely satisfactory from a theoretical point of view and it has never been proved that the cell action will take place in a large scale cell of the same constitution. Though this theory has certain very attractive features, it has never been generally accepted.

With the theory in this stage it reached somewhat of an impasse. The general photographic effects were well enough known and the *concentration-speck theory* served to connect these facts better than any other theory. However, not enough was known about the mechanism of the process from an atomic point of view. Significant advances in this direction have come only very recently and are a result largely of the recent theoretical and experimental advances in our knowledge of the solid state. The application of quantum mechanics in studies of the solid state has brought about marked changes in our ideas about the electronic behavior of crystalline solids.[27] Through this work, an understanding of the behavior of metals, insulators, and semiconductors has been given for the first time, and straightforward explanations of various properties such as metallic conduction, photoconductance, and contact rectifiers have been forthcoming.

Valuable information has also been obtained from recent experimental studies of the solid state. Of paramount importance for the present subject have been the extensive studies carried out by R. W. Pohl[28] and his co-workers in Göttingen on the electronic and ionic properties of insulating crystals, particularly of the alkali- and silver-halide types. These studies may be said to form the experimental basis for the further developments in latent-image theory to be discussed in the remaining part of this paper.

The Gurney-Mott Theory

In a recent paper[29] (1938) Gurney and Mott proposed a new theory of latent-image formation which appears to give a more adequate explanation of all the phenomena connected with the latent image than any previous theory. This theory is in good accord with the *concentration-speck theory* proposed earlier by Sheppard, Trivelli, and Loveland, and in fact strengthens this former theory by supplying an underlying mechanism for it that is in every way in strict accord with modern-day views of atomic physics.

The Gurney-Mott theory assumes from the outset that the latent image itself is a submicroscopic speck of metallic silver. Its great achievement lies in the straightforward explanation given for the manner in which silver can be formed only at certain discrete points on the surface of the grain while at the same time allowing for the fact that the light absorption takes place at random points all over the grain. In this new theory, the authors make use of the two properties of silver bromide: photoconductivity and electrolytic conductivity, which we shall now discuss in some detail.

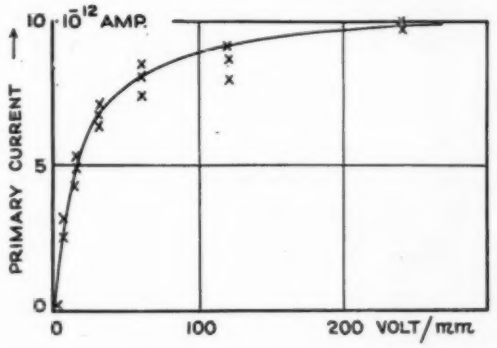

FIG. 3. Current-voltage curve of photoconductance effect for AgBr under constant illumination (Lehfeldt).

Photoconductivity

As stated earlier, silver bromide is known to exhibit the property of photoconductance. According to quantum mechanics,[27] this condition

comes about in an insulating crystal by virtue of electrons being raised from a lower energy band of the crystal, which is completely filled with electrons, to an upper empty band commonly referred to as the conduction band. An electron in the conduction band of the silver bromide crystal may be viewed as shared by all the Ag^+ ions of the lattice and as continually moving about from one Ag^+ ion to another. Such an electron behaves as a free conduction electron of a metal and in the presence of an electric field gives rise to electronic conduction. There is always a certain probability that such a free electron in the crystal will recombine with its "positive hole" and thus transform the crystal back to its insulating state.

From the experimental side, the photoconductance effect in insulating crystals has been studied mainly by Pohl[30] and his co-workers in Göttingen. In measurements of photoconductivity, the crystal is set up between electrodes with a known potential between them and the total current through the crystal measured on illumination. A voltage-current curve obtained by Lehfeldt[31] for silver bromide under constant illumination is shown in Fig. 3. It is seen that the curve rises at first, linearly with the voltage, and then approaches asymptotically to a maximum saturation value at high voltage. For an understanding of this behavior it should be pointed out that the contribution to the electric current by each electron released by light depends not alone upon its charge but also upon the fractional distance between electrodes traveled by that electron. The horizontal part of the curve of Fig. 3 is attributed to the fact that, at high voltages, electrons released by light are pulled all the way to the positive electrode, thereby producing saturation. At lower voltages, it must be concluded that the electrons are caught in some manner before reaching the electrode. Lehfeldt[31] has studied this effect in the silver halide crystals and has found that crystals which contain colloidal particles of silver require higher electric fields for saturation. The conclusion from these results is that colloidal silver specks act as traps for the electrons and thereby cut down the average distance traveled by these electrons. According to Gurney and Mott[29] the trapping of electrons by colloidal metal particles is to be explained by a consideration of the energy diagrams of the metal and silver salt. Such a diagram is given in Fig. 4. The energy of a free conduction electron in silver bromide lies in the upper conduction band. If the lowest energy level of this band lies above the highest filled conduction levels of the metal as illustrated, then an electron passing from the silver bromide to the metal will descend through the potential step ΔE and become trapped.

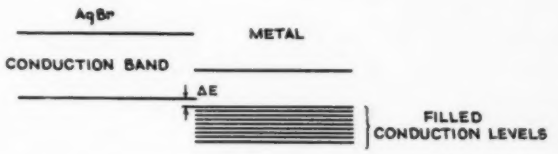

FIG. 4. Electronic energy bands of AgBr and adjoining silver metal.

Electrolytic Conductivity

The other property of silver bromide which is essential for the Gurney-Mott theory of the latent image is that of conductivity by ionic migration. Measurements of ionic conductivity of the silver halides have been carried out by a number of investigators and it is a well-known fact that these materials exhibit relatively large conductivity even at room temperature. Tubandt[32] and co-workers showed that the conductivity of the silver halides is due principally to the movement of the Ag^+ ions. The conductivity varies rapidly with temperature and, according to measurements by Lehfeldt,[33] is about 10^{-8} ohm^{-1} cm^{-1} at room temperature. For a long time it was not clear how Ag^+ ions could move through the crystal lattice so readily as indicated by the magnitude of the observed currents. The first satisfactory picture to show how this could take place was given by Frenkel[34] and has been worked out more recently by Jost,[35] Koch, Wagner, Schottky, and others.[36] According to this picture, the ionic conductivity of the silver halides comes about by virtue of Ag^+ ions dislodged by heat motion from their regular lattice positions and removed to interstitial positions. This is illustrated in Fig. 5. That the Ag^+ ions, and not the Br^- ions, are pushed into the interstitial positions is attributed to the smaller size of the positive Ag^+ ion. The ionic conductivity of silver bromide is ascribed to the movement of these interstitial Ag^+ ions and to the movement

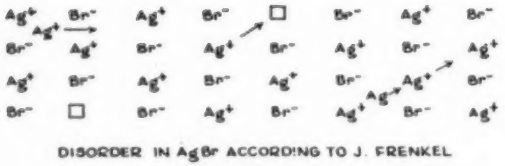

FIG. 5. Model to illustrate electrolytic conductivity in AgBr.

of the vacant places left in the lattice. How this occurs is clear from Fig. 5. The interstitial ions move either to other interstitial positions or into vacant positions in the lattice. If the latter takes place, the holes are said to move by replacement conduction.

Direct Print-Out Effect

As mentioned earlier, the direct photodecomposition of silver bromide into metallic silver and bromine occurs in the grains of a photographic emulsion as well as for gelatin-free silver bromide, and furthermore, according to the work of Eggert and Noddack, the law of quantum equivalence holds. It should be further pointed out that the silver formed in the photochemical decomposition of silver bromide is always found as colloidal specks, whereas it is fairly certain that the light active in producing the silver is absorbed all over the surface of the silver bromide grain. We shall first consider the theory put forward by Gurney and Mott in connection with the direct print-out effect.

According to measurements of photoconductivity in silver bromide, for each quantum of light absorbed by a silver bromide grain, there is released one electron which can move about freely in the crystal. Furthermore, evidence has been given to show that these electrons can be trapped on metallic silver specks in the lattice. If the assumption is made that there is a minute amount of silver in colloidal form present to begin with, electrons liberated by light will become trapped on such specks and charge them negatively. This negative charge will set up an electrostatic field* within the grain to attract positive charges. Gurney and Mott postulate that, under the action of this field-free Ag^+, ions in the lattice will move up to the speck and neutralize the electron there to form silver atoms. In this way it is seen how the speck can grow by one atom of silver for each quantum of light absorbed. By repetition of this process, a speck can presumably grow as long as there is room for it to do so. It is to be noted that this theory allows for the fact that one atom of silver is formed for each quantum of light absorbed, and is thus in accord with the condition of quantum equivalence. Also, the theory furnishes a mechanism whereby light absorbed all over the grain can produce silver atoms only at certain discrete points.

The Latent Image

The description just given applies to the case of the direct photolysis of silver bromide when there are present initially colloidal specks of silver. The latent-image problem differs from this case in that it must be shown how it is possible for the silver speck to begin to grow. To account for this in the case of the latent image, Gurney and Mott propose that the silver sulfide specks discovered by Sheppard can play the role of electron traps in the same way as colloidal silver specks. If the silver sulfide specks can trap electrons and become negatively charged, then Ag^+ ions will be attracted to these specks and the silver of the latent image can form in precisely the same way as was outlined in the case of the print-out effect.

The new theory of latent-image formation proposed by Gurney and Mott has many points in its favor. Fundamentally, it is founded on well accepted concepts of atomic physics. It has succeeded in explaining some of the more puzzling features of the latent-image problem which former theories have been unable to do. Furthermore, it has shown itself capable of accounting for the principal auxiliary effects connected with the latent-image formation such as reciprocity law failure and the Herschel effect, which will be discussed later.

The best experimental support for the theory of latent-image formation given by Gurney and Mott has been obtained by means of experiments at low temperature. We shall now give some of these results and show how they confirm the theory.

* The electric field set up in a silver bromide grain due to an electron at a distance equal to the diameter of a grain (0.5×10^{-4} cm) amounts to approximately 90 volts/cm.

Effect of Temperature

Some experimental results[40] showing the effect of temperature on emulsion sensitivity are given in Fig. 6. In the upper left quadrant are shown two H and D curves made at room temperature and liquid-air temperature, respectively. The great drop in sensitivity at the low temperature is to be noted. The curves given in the other three quadrants show the results of two series of intermittent exposures, both of which were made at liquid-air temperature. In the (A) series the emulsion was warmed up to room temperature for a brief interval during the dark period between the intermittent flashes, while in the (B) series the emulsion was maintained at the low temperature during the dark periods. The (B) curves of Fig. 6 show that there is no effect introduced by interrupting the exposures made at liquid-air temperature, providing the low temperature is maintained during the dark periods. The (A) curves show that the same procedure produces a marked effect when the emulsion is warmed to room temperature between the intermittent flashes. Subdivision of the exposure into two 80-second exposures (Fig. 6(b)) is seen to increase materially the photographic effect. Breaking the exposure into four 40-second exposures (Fig. 6(c)) and warming up between flashes still further increases the photographic effect, and carrying the process a step further to eight 20-second exposures (Fig. 6(d)) raises the sensitivity up to a value comparable with that at room temperature. These experiments illustrate clearly that some action important in latent-image formation occurs in the warm-up periods between flashes while no exposure is being applied.

Let us see how the above experiments fit in with the Gurney-Mott theory of latent-image formation. This theory supposes the latent-image formation to consist of two parts: (1) a primary process consisting of release of photoconducting electrons and their trapping by sensitivity specks, and (2) a secondary process consisting of an electrolytic migration of Ag^+ ions to the negatively charged sensitivity specks. The former is an electronic process and has been shown by Lehfeldt[31] to be little affected by temperature down to $-186°C$. The latter process, however, consisting of ionic conductivity, is known to be very dependent upon temperature.[38] According to the Frenkel-Jost model to account for ionic conductivity, the number of Ag^+ ions available for producing conductivity as well as the mobility of these ions is dependent entirely upon temperature motion. At the temperature of liquid air, mobility of the ions would be so low that it may be considered zero for the photographic process as outlined. What then is the effect to be expected on the latent-image process? At this temperature it may be assumed[31] that one electron is released per absorbed quantum and that the first few electrons liberated within a grain are trapped on the sensitivity specks. However, if no ionic conductivity can take place in the crystal, these negatively charged specks will not be neutralized and a condition will very soon arise whereby electrons will be repelled* by the sensitivity specks. It may be postulated that under these conditions some of the free electrons will recombine with their parent bromine ions and become lost for the latent-image process. This will account for the drop in sensitivity at very low temperatures. The experimental results of Fig. 6(a) seem to be in accord with this interpretation.

A more accurate test of the Gurney-Mott theory of latent-image formation is afforded by the interrupted exposures shown in Fig. 6. These experiments show that some process vital to the latent-image process occurs during the warm-up periods between exposures. The results are explained by the Gurney-Mott theory as follows: Assume that the first flash leads to the trapping of several electrons on a sensitivity speck. The emulsion being at liquid-air temperature, no Ag^+ ions can move up to the speck and neutralize this

* The fate of these repelled electrons is not certain. It has been suggested (reference 39) that these electrons may become caught in shallow energy levels in the crystal and then be released when the emulsion is warmed up for development. Good evidence for this view is furnished by experiments on secondary current phenomena which show that the silver halide crystal can be rendered into an excited state by illumination at low temperatures. However, the important point seems to be the temperature at which this excited state is destroyed. If this is below the value for which appreciable ionic conductivity can occur, then the result will still be the same as though the electrons had never been caught in the shallow traps. From experiments by Lehfeldt (reference 31) it appears that the temperature at which the excited state is destroyed is of the order $-100°C$.

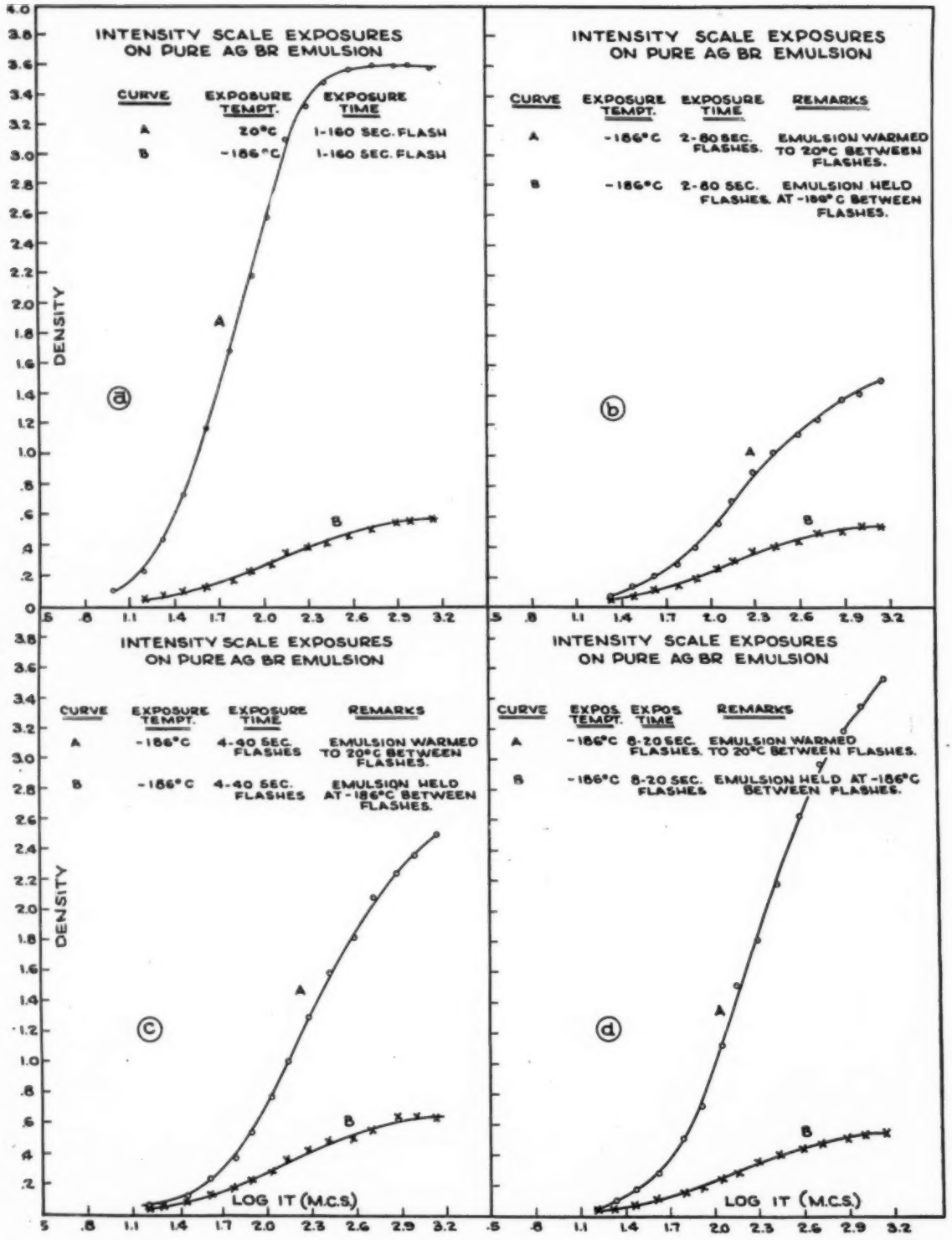

FIG. 6. Curves illustrating effect of making interrupted exposures at liquid-air temperature and warming up the emulsion between exposure periods. The curves *a*, *b*, *c* and *d* show the effect of breaking the exposure time into smaller and smaller intervals. The *A* curves are for cases where the emulsion is warmed to 20°C between flashes, and the *B* curves are for cases where the emulsion is held at −180°C between flashes.

charge. Warming up of the emulsion in the dark period following the exposure permits ionic movement and neutralization of the charge to take place. A further flash exposure at low temperature will now add several more electrons to the

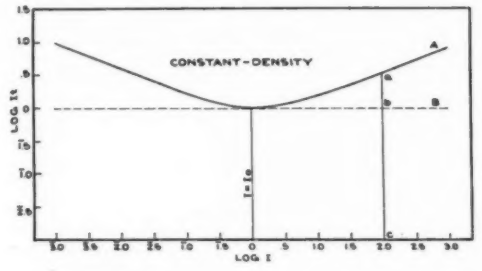

FIG. 7. Typical reciprocity law failure curve for a photographic emulsion.

speck. Upon warming up again, further Ag^+ ions will diffuse to the speck. As a given exposure is broken into more and more flashes, this process is repeated more and more times, and since the greater the number of flashes the smaller the negative charge that need be added to the speck at each flash, the less is the unneutralized charge placed on the speck at each flash. Since, for smaller unneutralized charges, fewer electrons will be lost for the latent-image process, the photographic effect should increase with the number of flashes into which the total exposure is subdivided. The experimental results of Fig. 6 have shown that it is possible to separate the primary and secondary process of latent-image formation and to study each separately. Insofar as it has done this and further shown that the primary process is independent of temperature and the secondary process is dependent upon temperature, it affords evidence in favor of the Gurney-Mott theory.

Reciprocity Law Failure

The Bunsen-Roscoe reciprocity law[40] for photochemical reaction states that the product of a photochemical reaction is dependent simply on the total energy employed, that is to say, on the product of intensity and time, and is independent of these two factors separately. It is a well-known fact[41] that photographic materials do not obey this law, but show a decided dependence on the intensity level at which the exposure is made. In Fig. 7 is shown a typical curve representing the departure from the reciprocity law for a photographic emulsion. This curve represents the amount of exposure required to produce a constant density as a function of the intensity. It is characterized by a minimum corresponding to an optimum intensity, this being the intensity level for which a given photographic effect is produced by the smallest amount of light energy. The curve rises at intensity values above and below optimal, these departures from a straight horizontal line being commonly referred to as the high and low intensity failures, respectively. Experimental evidence exists to show that these two effects at the two extremes of intensity arise from separate causes. The chief evidence for this consists of measurements of reciprocity law failure at different temperatures, according to which the high and low intensity effects are found to have opposite temperature coefficients. A series of reciprocity failure curves covering the range of temperatures, $+50°C$ to $-75°C$ is shown in Fig. 8. It may be seen that as the temperature is lowered from $+50°C$, the upturn of the curve at

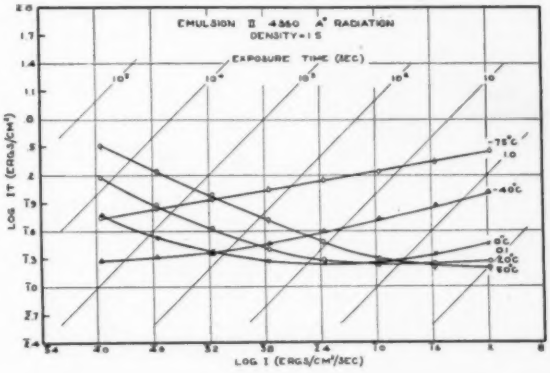

FIG. 8. Curves illustrating effect of temperature variation on the reciprocity law failure.

low intensities dies out while the high intensity end of the curve moves upward. The net result of these two effects on the reciprocity curve is a shift of optimal intensity to lower values. We shall consider now the high and low intensity effects separately.

HIGH INTENSITY EFFECT

On the basis of the theory of latent-image formation proposed by Gurney and Mott the

reciprocity law failure at high intensity can be well accounted for. According to this theory the high intensity effect is attributable to the sluggishness of the secondary process of latent-image formation consisting of the Ag^+ ion diffusion. For exposures at high intensity it is supposed that the diffusion of Ag^+ ions in silver bromide cannot keep pace with the primary, or electronic, part of the latent-image process. This would prevent immediate neutralization of the electronic charges as they are trapped on the sensitivity specks. The negative charge resulting on the specks will repel further electrons and thereby limit the subsequent rate of trapping of electrons to that at which Ag^+ ions can reach the speck. In this way some electrons liberated by light will become lost for the latent-image process and a drop in sensitivity will result as described previously. With increasing intensity of the exposing light, this effect becomes more pronounced resulting in the loss of speed with increasing intensity level as is observed. The shift upward of the high intensity end of the reciprocity failure curve with lowered temperature is also understandable in the light of this discussion. As the temperature is lowered, the mobility of the Ag^+ ions is lowered, thus slowing up still further the rate at which these ions can diffuse to the specks. Thus in the region of high intensity where exposure times are short and ionic mobility becomes an important factor in emulsion sensitivity, reduction of temperature results in lowered sensitivity. This is in accord with the shift upward of the high intensity end of the reciprocity failure curve observed at lowered temperature. It might be added that in this region, a decrease of temperature should have the same effect as an increase of light intensity, since either would act effectively to slow up the ionic mobility relative to the rate of charging up of the speck. This, in fact, is what is observed as may be seen in Fig. 8.

When the temperature is lowered to $-186°C$, the reciprocity law failure for photographic emulsion is found to have disappeared[42] entirely. This is brought out in the results of Fig. 9 which shows reciprocity failure curves for 20°C, $-78°C$, and $-186°C$. The curve for $-186°C$ is seen to be horizontal showing no effect of intensity level on sensitivity. This disappearance of reciprocity law failure at low temperature may be considered as further evidence in favor of the Gurney-Mott theory. At the temperature $-186°C$, ionic mobility in silver bromide is so low that it must be assumed that no movement of Ag^+ ions can take place during the time of an ordinary exposure. Experimental evidence for this from the photographic standpoint has been given by the curves of Fig. 6 pertaining to interrupted exposures at low temperature. Thus at the temperature $-186°C$, it may be assumed that the electronic process alone takes place during the exposure to light and that the secondary ionic process does not occur until the photographic grain is warmed up. On the basis of this picture, the photographic process would therefore cease to be a function of the intensity level of the exposing light at the low temperature.

Low Intensity Effect

The failure of the reciprocity law at low intensity signifies a drop in efficiency in the formation of the latent image with lowered intensity. From Figs. 8 and 9 it may be seen that this effect is diminished by a decrease in temperature. This experimental fact has led to the postulate[27, 29, 43]

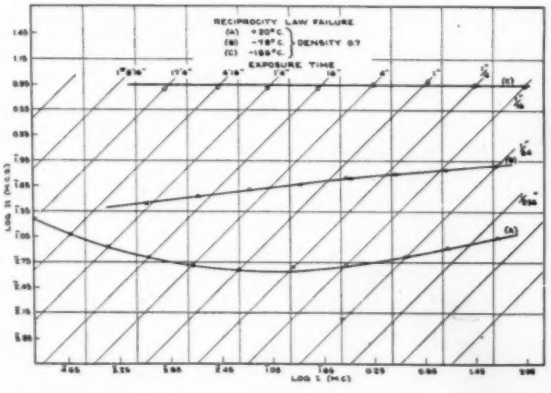

Fig. 9. Curves illustrating effect of temperature variation on the reciprocity law failure.

that the low intensity reciprocity law failure arises from a regression of the latent-image speck by thermal motion. To account for the fact that the effect increases with lowered intensity it is necessary to assume that this regression takes place more readily in the initial stages of formation of the speck than in the later stages. Thus, for a low intensity exposure, in which case the

speck forms slowly and may exist for some time as a speck of only a few silver atoms, better opportunity is afforded for the speck to be broken up. This thermal disintegration of the speck is supposed to proceed by ejection of an electron from the speck into the surrounding silver bromide crystal by heat motion, followed by the diffusion away of a Ag^+ ion. Since the explanation rests essentially on the thermal ejection of electrons, the observed suppression of this effect with lowered temperature may be understood.

The idea that the reciprocity law failure at low intensities results from disintegration of the latent-image speck in its initial stages of formation has some support in the following experiment:[44, 45] An emulsion was given a series of equal energy exposures, each exposure consisting partly of high intensity (H.I.) and partly of low intensity (L.I.) light. The intensity level used in the H.I. part was near optimal, while that of the L.I. part was lower by a factor of 1000. The results of a series of such exposures in which the relative proportions of H.I. to L.I. were varied over the range zero to one, are shown in Fig. 10. The upper curve of the loop corresponds to the condition that the H.I. part of the exposure was made first, while the lower curve corresponds to the condition that the L.I. part of the exposure was made first. For both curves the relative proportions of H.I. to L.I. exposure were varied through the same steps as indicated on the diagram at the bottom of the figure. The reciprocity law failure for the emulsion, between the intensity levels H.I. and L.I., is shown by the difference in height between the extreme left point (all H.I. exposure) and the extreme right point (all L.I. exposure). The different courses of the two curves between these two points are attributable to the difference in the time order of the exposures. It is seen that if the H.I. part of the exposure is put on first, the L.I. part of the exposure is always rendered more efficient. In fact, for the case illustrated, it may be seen that if the H.I. exposure is given first and amounts to as much as one-fourth the total exposure, the L.I. part of the exposure is rendered just as efficient as the H.I. part. On the other hand, if the order of the exposure is reversed, the L.I. part being given first, the drop in efficiency of

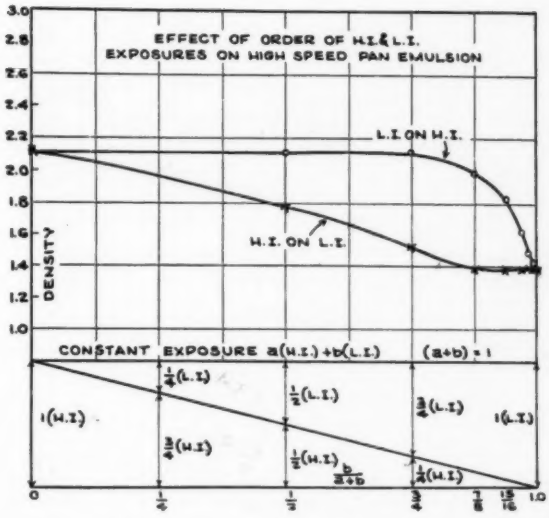

FIG. 10. Effect of equal energy, mixture-exposures of part high intensity and part low intensity given in different time order.

the L.I. exposure is very marked. The interpretation that has been given these results is that the reciprocity law failure at low intensity takes place principally in the initial stages of exposure while the speck is still small.

The Intermittency Effect

A photographic effect closely associated with the reciprocity law failure is the so-called "intermittency effect." The effect of an exposure given in a number of discrete installments is, in general, different from that produced by a continuous exposure of the same energy. The effect of the intermittent exposure may be greater than, less than, or equal to that of an equal energy continuous exposure, depending upon the intensity levels at which the exposures are made.

From recent work on the intermittency effect[46] it is now recognized that this effect is not a separate and independent phenomenon but is merely an aspect of reciprocity law failure. The effect produced by an intermittent exposure is found always to lie between the effects produced by two continuous exposures: one of intensity equal to that of the flash period and the other of intensity equal to the average intensity of the intermittent exposure. A continuous exposure and an intermittent exposure of the same average intensity and over-all duration become equal in their effects when the frequency of flash sur-

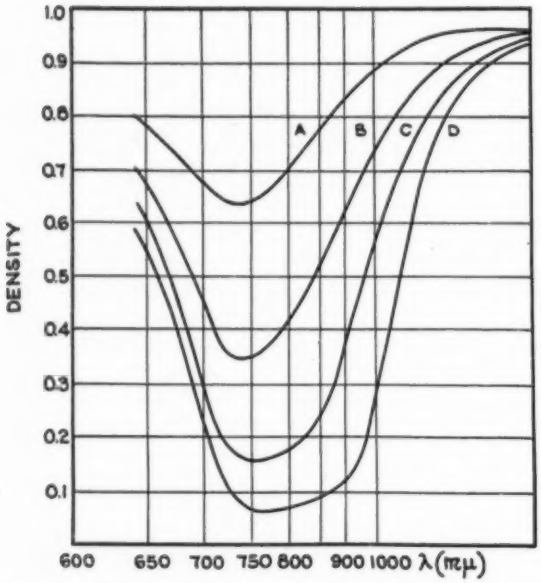

FIG. 11. The spectral distribution of the Herschel effect with increasing exposure (Bartelt and Klug).

passes a certain critical value, which varies with the intensity level. In this respect the photographic emulsion behaves like the eye, though undoubtedly for very different reasons. We can say from general physical considerations[47] that the critical frequency of flash will correspond to the condition that one grain receives on the average approximately one quantum of light per flash of the intermittent exposure. In this way it is seen that the critical frequency will vary with the size of the emulsion grain and the intensity of the exposing light.

The Herschel Effect

If an emulsion, which has been previously exposed to blue radiation, is subsequently exposed to infra-red light before it is developed, some of the effect of the original blue light exposure is found to be erased. In other words, the red light is capable of destroying the latent image to some extent. This effect discovered by Sir J. Herschel[48] is known after its discoverer as the Herschel effect.

The Herschel effect as a function of the wave-length of the reversing radiation is shown by the results of Fig. 11 taken from work by Bartelt and Klug.[49] These curves show the decrease in density resulting from increasing amounts of red light exposure. The maximum effect is seen to occur at approximately wave-length 750 mμ; however, radiation over a wide band of wave-length extending from 650 mμ to beyond 1000 mμ is capable of reversal action. In spite of the great amount of experimental work that has been done on the subject,[50] the process is still not thoroughly understood and there is not complete agreement among workers as to the explanation of this phenomenon. Some of the most important information relative to the Herschel effect has been obtained from studies with large single crystals of silver bromide. We shall therefore give some of these results and show how they have thrown light on the Herschel effect.

It is well known that the silver halides develop a coloration when exposed to light absorbed in their characteristic absorption bands. Hilsch and Pohl[51] studied this photochemical coloration in large single crystals of silver bromide with especial regard for its relation to the photographic latent image. They found that the coloration is due to an induced absorption band with its maximum at wave-length 700 mμ. In Fig. 12 are given curves taken from Hilsch and Pohl's paper showing this induced absorption band along with the characteristic absorption band of silver bromide. The curve (a) corresponds to curve (a′) multiplied by a factor 10^6 in order to put it on the same scale as curve (b). In their studies of this absorption band, Hilsch and Pohl took care to keep the concentration of photo-product at about the same level as is obtained in the normally exposed photographic emulsion. This was done by controlling the wave-length and amount of exposure given the large crystal. Concentrations of photo-product of this magnitude are not measurable in layers of the thickness of the photographic emulsion but become so when produced in crystals of thickness 1 mm, as used by Hilsch and Pohl. These workers found that if one of these crystals, which had been previously colored by an exposure to light in the characteristic absorption band, was exposed to longer wave-length light falling within the induced absorption band, the induced absorption band was bleached, and preferentially so, in the wave-length region of the bleaching light. From these experiments, Hilsch and Pohl concluded that the induced absorption band produced by the short wave-

length radiation corresponded to the latent photographic image and that the bleaching of this band by long wave-length light corresponded to the Herschel effect in the photographic case. The great width of the induced absorption band in single crystals and its nondependence upon temperature were interpreted to mean that this absorption band arises from colloidal particles of silver of a great variety of sizes. Each particle size has its own absorption band and the whole band is made up of a superposition of these separate narrow bands. It now appears that this is substantially a correct view, but the question of the mechanism of light absorption by the particles in such a way as to lead to their destruction is still not completely answered. It has been suggested that this takes place through a resonance type absorption by the metallic particles. That is, the metal specks are supposed to resonate to a given wave-length radiation and absorb energy as a damped Hertzian oscillator. For the larger colloidal particles of Ag dispersed in AgBr and AgCl (such for example as used for study of the Weigert effect), evidence has been given[52] to show that this is probably a

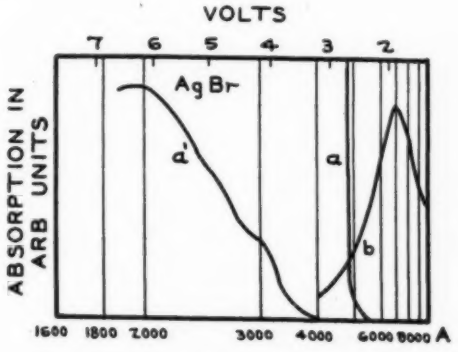

FIG. 12. Characteristic absorption band (*a* and *a'*) and induced absorption band (*b*) for AgBr (Hilsch and Pohl).

correct view. At least, the size of the particles is such that according to the theory they could resonate to wave-lengths for which absorption is observed. However, for the colloidal particles of the size of the latent-image specks, the theory of resonance absorption does not seem to fit in very well with the observed facts. This point has been discussed by Berg[53] who points out that the dimensions of the latent-image specks are such that they could not possibly resonate with the wave-length light absorbed. What appears to be a more likely explanation of the absorption by the colloidal silver specks (at least those of latent-image size) is that proposed by Gurney and Mott.[29] They attribute the absorption of long wave-length light by the latent-image silver speck to photoelectric ejection of electrons from the silver into surrounding silver bromide. In order to account for the destruction of the speck, which presumably takes place in the Herschel effect, it is assumed that a Ag^+ ion is pushed after the electron by the positive charge left on the speck. The fact that the photoelectric effect as described here would be little influenced by temperature would account for the nondependence of the position of the absorption band upon temperature. To account for the broad width of the absorption band, it is necessary to assume that the energy required to eject electrons from a small metallic speck is a function of the size of the speck. It is not unreasonable that this is the case with these small particles.

Experimental evidence[54, 55] has been obtained which seems to support the foregoing explanation of the Herschel effect. This work consists of measurements of the Herschel effect under varied temperature conditions. Some of the experimental results obtained in this way are shown in Fig. 13. The straight horizontal line in these diagrams represents the density obtained on an emulsion by a primary flash exposure to white light. The points indicated with circles represent the density values obtained from a subsequent exposure to infra-red light superposed on the primary exposure. The abscissa values pertain to the log of the exposure to the infra-red light.

The curves of Fig. 13(a) show the normal Herschel effect in which both white light and infra-red exposures were made at room temperature (20°C). In Fig. 13(b) the white light exposure was made at 20°C and the infra-red exposure was made after the emulsion was cooled to −186°C. No Herschel effect was obtained under these conditions. Fig. 13(c) shows the results of an experiment in which the white light exposure was made at −186°C and the infra-red exposure was made on the emulsion after it was warmed up to 20°C. A Herschel

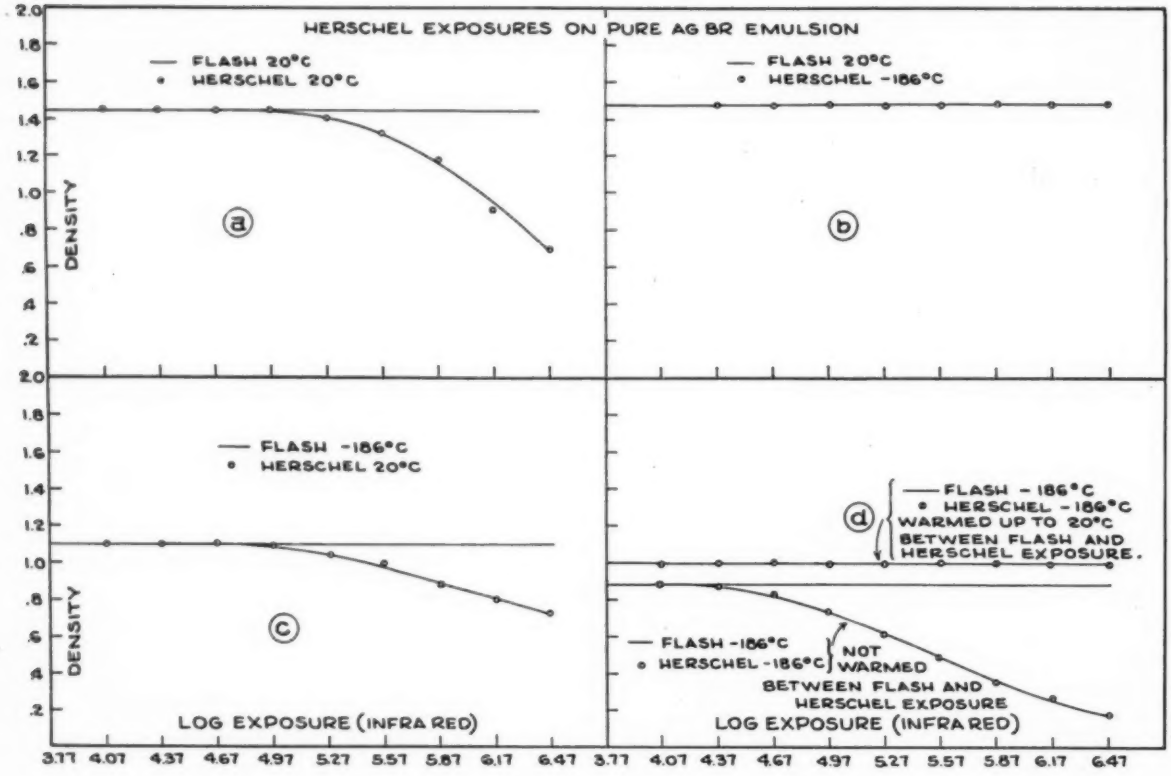

FIG. 13 Curves illustrating the Herschel effect under varied temperature conditions.

effect was obtained again in this case. Fig. 13(d) shows the results of two experiments. In each experiment, both exposures were made at −186°C. However, in the one case the emulsion was warmed up to 20°C between the primary white exposure and the infra-red exposure, while in the other case the emulsion was maintained at −186°C between exposures. It may be seen that when the emulsion was not warmed up between exposures, a large Herschel effect was obtained while in the case where the emulsion was warmed up between exposures no Herschel effect was obtained.

The foregoing experimental results afford evidence in favor of the postulate of Gurney and Mott that the destruction of the latent image speck is due to the ejection of electrons followed by diffusion away of a Ag^+ ion. The experiment made at room temperature (Fig. 13(a)) has no appreciable bearing on the matter, but it is not in disaccord with the postulate. The results of the other experiments can all be accounted for by the proposed mechanism provided the assumption is made that no Ag^+ ion diffusion can occur at −186°C. Thus, in Fig. 13(b), the normal latent image is formed by an exposure at room temperature. In the exposure to the infra-red light at low temperature, we can assume that the electrons will be ejected, but if Ag^+ ions cannot follow, the speck will not disintegrate and the electrons will be drawn back again by the positive charge on the speck. Thus the speck will remain intact after withdrawal of the infra-red stimulus. The results of the experiment of Fig. 13(c) are very much like those of Fig. 13(a). The Herschel exposure made at room temperature can diminish whatever latent-image specks there are present. The results of Fig. 13(d) afford perhaps the most decisive evidence of all. In line with the original assumption of no Ag^+ ion diffusion at −186°C, it must be supposed that the true latent image is not formed by the white light exposure at this temperature. Instead only the electronic part of the process will occur, and the resulting condition is a "potential" latent image consisting of elec-

trons trapped on the preexisting sensitivity specks. Now, if a subsequent infra-red exposure is given while the emulsion is still at the low temperature, this potential latent image is readily destroyed. Presumably, this occurs by ejection of the electrons from the speck. On the other hand, if the emulsion is warmed up to room temperature after the white light exposure and before the infra-red exposure, the full latent-image specks form. Then, upon taking the emulsion down to −186°C, the latent image cannot be erased by the infra-red radiation for the same reason as discussed for Fig. 13(b). These experiments speak very strongly in favor of the existence of a primary and secondary process in the Herschel effect. The former is apparently independent of temperature, while the latter is very dependent on temperature. These results accordingly give confirmation of the proposal by Gurney and Mott that the Herschel effect consists of a primary (photoelectric) process and a secondary (electrolytic) process.

Bibliography

1. For a description of the preparation of photographic emulsion, see B. H. Carroll, J. Chem. Education **8**, 2341 (1931).
2. M. Biltz, Physik. Zeits. **36**, 559 (1935).
3. *Andrees Story* (Viking Press, New York, 1930).
4. E. J. Hartung, J. Chem. Soc. (London) **125**, 2198 (1924); **127**, 2691 (1925); **129**, 1349 (1926); E. Mutter, Zeits. f. Wiss. Phot. **26**, 193 (1928/29); H. Kieser, Zeits. f. Wiss. Phot. **26**, 1 (1928/29).
5. P. P. Koch and H. Vogler, Ann. d. Physik **77**, 495 (1925).
6. J. Eggert and W. Noddack, Sitzgeb. Preuss. Akad., 631 (1921); 116 (1923); Zeits. f. Physik **20**, 299 (1923).
7. E. R. Bullock, *Chemical Reactions of the Photographic Latent Image* (Monograph No. 6, Eastman Kodak Co., 1927).
8. Arago (see J. M. Eder, Ausf. Handbuch Phot. Vol. II, No. I, 2nd edition, p. 110 (1895)).
9. Carey Lea, Am. J. Science (**3**) **33**, 349 (1887).
10. Wi. Ostwald, Lehrb. allg. Chem. II, **1**, 1078 (1893).
11. R. Abegg, Archiv. Wiss. Phot. **1**, 109 (1899).
12. Lüppo-Cramer, *Kolloid Chemie und Photographie* (Steinkopff, Dresden, 1st Ed., 1908); also Phot. Korr. **44**, 327 (1907).
13. C. E. K. Mees and S. E. Sheppard, *Investigations of the Theory of the Photographic Process* (Longmans, Green & Co., 1907), pp. 69–91.
14. M. B. Hodgson, J. Frank. Inst. **184**, 705 (1917).
15. T. Svedberg, Phot. J. **62**, 186 (1922).
16. F. C. Toy, Phil. Mag. **45**, 715 (1923).
17. W. Clark and F. C. Toy, Phil. Mag. **44**, 352 (1922).
18. E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, J. Frank. Inst. **194**, 485 (1922); S. E. Sheppard and E. P. Wightman, J. Frank. Inst. **195**, 337 (1923); S. E. Sheppard, E. P. Wightman and A. P. H. Trivelli, J. Frank. Inst. **196**, 779 (1923); **198**, 507 (1924); **198**, 629 (1924).
19. S. E. Sheppard, Phot. J. **65**, 1 (1925).
20. S. E. Sheppard and E. P. Wightman, J. Frank. Inst. **195**, 337 (1923).
21. W. Clark, Phot. J. **48**, 91 (1924).
22. W. Clark, Brit. J. Phot. **74**, 227 (1927).
23. S. E. Sheppard, A. P. H. Trivelli and R. P. Loveland, J. Frank. Inst. **200**, 51 (1925).
24. F. C. Toy, Nature **120**, 441 (1927); **121**, 865 (1928).
25. W. Vanselow and S. E. Sheppard, J. Phys. Chem. **33**, 331 (1929); S. E. Sheppard, W. Vanselow and V. C. Hall, J. Phys. Chem. **33**, 1403 (1929).
26. A. P. H. Trivelli, Phot. J. **68**, 67–72 (1928).
27. For a review of this work see F. Seitz and R. P. Johnson, J. App. Phys. **8**, 84 (1937); **8**, 186 (1937); **8**, 246 (1937).
28. R. Hilsch and R. W. Pohl, Zeits. f. Physik **64**, 606 (1930); R. W. Pohl, Proc. Phys. Soc. (Extra Part) No. 274, **49**, 3 (1937).
29. R. W. Gurney and N. F. Mott, Proc. Roy. Soc. **A164**, 151 (1938).
30. R. W. Pohl, Proc. Phys. Soc. **49** (Extra Part) 3, No. 274 (1937).
31. W. Lehfeldt, Nach. Ges. Wiss. Gött. **1**, 171 (1935).
32. C. Tubandt, *Handbuch der Exper. Physik*, Vol. II (Leipzig, 1932); C. Tubandt and S. Eggert, Zeits. f. Anorg. Allgem. Chemie **110**, 196 (1920).
33. W. Lehfeldt, Zeits. f. Physik **85**, 717 (1933).
34. J. Frenkel, Zeits. f. Physik **35**, 652 (1926).
35. W. Jost, J. Chem. Phys. **1**, 466 (1933).
36. E. Koch and C. Wagner, Zeits. f. physik. Chemie **38B**, 295 (1927); C. Wagner and W. Schottky, Zeits. f. physik. Chemie **11B**, 163 (1930).
37. J. H. Webb and C. H. Evans, J. Opt. Soc. Am. **28**, 249 (1938). See also results by W. F. Berg and K. Mendelssohn, Proc. Roy. Soc. **A168**, 168 (1938); W. F. Berg, Trans. Faraday Soc. **35**, 445 (1939).
38. W. Lehfeldt, Zeits. f. Physik **85**, 717 (1933).
39. W. F. Berg, Trans. Faraday Soc. **35**, 445 (1939).
40. R. Bunsen and H. E. Roscoe, Pogg. Ann. **108**, 193 (1876).
41. K. Schwarzschild, Astrophys. J. **11**, 89 (1900); W. de W. Abney, Phot. J. **18**, 254, 302 (1893–94); C. E. K. Mees and S. E. Sheppard, Phot. J. **43**, 48 (1903); L. A. Jones and E. Huse, J. Opt. Soc. Am. **7**, 1079 (1923); **11**, 319 (1925); L. A. Jones, E. Huse and V. C. Hall, J. Opt. Soc. Am. **12**, 321 (1926); L. A. Jones and V. C. Hall, J. Opt. Soc. Am. **13**, 443 (1926); L. A. Jones, V. C. Hall and R. M. Briggs, J. Opt. Soc. Am. **14**, 223 (1927); E. Kron, Pub. Astrophys. Obs. Potsdam, No. 67 (1913); J. R. Halm, Monthly Notices Roy. Astron. Soc., June, 1922, p. 473.

42. W. F. Berg and K. Mendelssohn, Proc. Roy. Soc. **A168**, 168 (1938); J. H. Webb and C. H. Evans, J. Opt. Soc. Am. **28**, 249 (1938).
43. N. F. Mott, Phot. J. **78**, 286 (1938).
44. C. E. Weinland, J. Opt. Soc. Am. **16**, 295 (1928).
45. J. H. Webb and C. H. Evans, J. Opt. Soc. Am. **28**, 431 (1938).
46. R. Davis, Sci. Papers Nat. Bur. Stand. **2**, 95, No. 528 (1926); E. A. Baker, Proc. Opt. Soc. Convention, 238, Part 1 (1926); A. E. Weber, Ann. d. Physik **45**, 801 (1914); F. Twyman and A. Harvey, Trans. Opt. Soc. London **33**, 1 (1931); H. E. Howe, Phys. Rev. **8**, 674 (1916); B. O'Brien, Phys. Rev. **33**, 640 (1929); B. O'Brien and V. L. Parks, Phys. Rev. **41**, 387 (1932); J. H. Webb, J. Opt. Soc. Am. **23**, 157 (1933).
47. J. H. Webb, J. Opt. Soc. Am. **23**, 157 (1933); L. Silberstein and J. H. Webb, Phil. Mag. **18**, 1 (1934).
48. J. Herschel, Athenaeum, Nr. 621, 1839.
49. O. Bartelt and H. Klug, Zeits. f. Physik **89**, 779 (1934); B. H. Carroll and C. M. Kretchman, Nat. Bur. Stand. J. Research **10**, 449 (1933).
50. For references to literature, see W. Leszynski, Zeits. f. Wiss. Phot. **24**, 275 (1927).
51. R. Hilsch and R. W. Pohl, Zeits. f. Physik **64**, 606 (1930).
52. A. E. Cameron and A. M. Taylor, J. Opt. Soc. Am. **24**, 316 (1934); M. Savostianova, IX Congrès International de Photographie, Paris, p. 94, 1935; M. Savostianova and A. Toporetz, Comptes rendus Acad. Sci. (U.R.S.S.) **2**, 228 (1934); W. Umrath, Dissertation, Göttingen, 1933; F. Lohle, Nach. Ges. Wiss. Gött. No. 43, 271 (1933).
53. W. F. Berg, Trans. Faraday Soc., Special Issue, **B5**, 889, April (1938).
54. W. F. Berg, Trans. Faraday Soc. **35**, 445 (1939).
55. J. H. Webb and C. H. Evans, J. Opt. Soc. Am. **28**, 249 (1938).

If you have no problems in your business, if you are perfectly satisfied with your product, your processes, and your costs in all respects, if you have no trouble from competition or other sources of worry, and are sure you are not going to have any for ten years to come, then you *may* not need research.

CHARLES F. KETTERING,
quoted in *Farm Chemurgic Journal*

The Response of Photographic Materials to Atomic Particles

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Introduction

WHEN radioactive research was in its infancy, the photographic plate was the main tool used in its study, but the development of ionization-chamber, counter and cloud-chamber techniques pushed the photographic technique into the background. Recently, however, it has been realized that for many problems in radioactivity and nuclear physics the photographic method would give information not obtainable so easily (if at all) by other methods. The recent revival of interest has led to much work on the laws of response of emulsions to high energy atomic particles such as alpha-rays, protons and deuterons and to attempts to improve the emulsions available for various types of studies in which they are involved.

In general, there are two types of nuclear phenomena which can be studied by the photographic method. (1) Those in which the density produced over sizeable areas is used, as for example in various types of radiographs or in evaluating the intensity of the radiation in terms of the photographic density produced. (2) Those in which the tracks due to individual particles are examined under a microscope. For the first, almost any photographic emulsion can be used while for the second, there are quite definite limits on the grain size and other characteristics of the emulsion—some imposed by the response of the emulsion and some by the technique used in the examination of the emulsion by the microscope, as for example, whether bright field or dark field illumination is to be used.

It was shown as early as 1910, by Kinoshita[1] that in the thin emulsions he studied, the number of grains made developable was equal to the number of alpha-particles incident on the emulsion for small photographic densities. With β-rays, on the contrary, 5 to 10 hits seem to be required to make a grain developable. Single β-rays will therefore not be expected to make tracks in such emulsions. Taking into account the relative ionizing powers of these two types of particles, it is indicated that the alpha-ray gives a grain several times as much energy as necessary to make it developable. Whether protons will produce visible tracks will, from this general reasoning, be uncertain—for a proton of the same range loses energy only one-quarter as fast as an alpha-particle. If an alpha-particle gave to a grain less than four times the energy necessary to make it developable, a proton of the same range would leave the grain unaffected. These considerations must be taken into account both in the study of the over-all density produced and in the possible production of tracks. It is possible to make emulsions in which no tracks are produced even for alpha-rays and others in which alpha-ray but no proton tracks are discernable.

I. The Density-Exposure Relation for Alpha-Rays—Reciprocity

1. Single Grain Layer Plates

The first sensitometric data on the response of a photographic emulsion was due to Kinoshita[1] who found that for single-grain-layer plates the relation

$$D = D_{\max}(1 - e^{-c_1 N}), \qquad (1)$$

in which N is the number of α-particles striking the plate in a time t; c_1 a probability constant; $D_{\max}$, the maximum density obtainable with the given emulsion and processing; D, the density corresponding to the given exposure N. The general form of this equation was confirmed by later work of Svedberg and Andersson[2] and still later by Eggert and Luft.[3]

2. Commercial Emulsions—Collimated Alpha-Rays

Wilkins and Wolfe[4] found that Eq. (1) holds also for commercial emulsions under certain

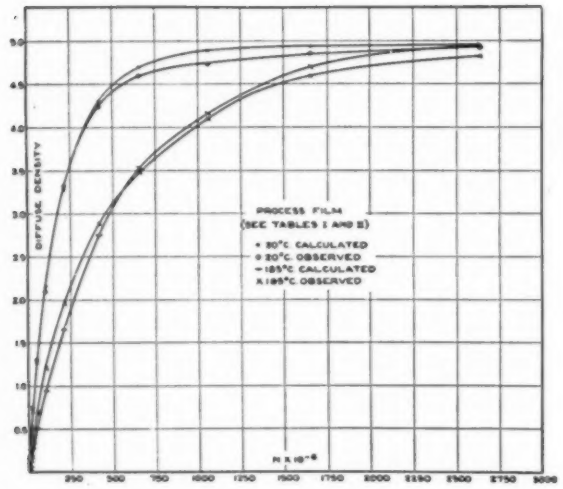


FIG. 1. Relation between density and number of alpha-particles.

Process Emulsion

Time of Development, 12 min. in 1 : 1 pyro soda at 20°C.

$D_m = 5.0$ $G_m = 2.71 \times 10^9$/sq. cm
Fog = 0.33 at 20° 0.30 at −185° $k = 10$ at 20° 3.6 at −185°
$\overline{\pi r^2} = 0.366\mu^2$ (determined by microscope) $k/G_m = 0.37 \times \mu^2$ at 20° C.

conditions, that is, with collimated α-rays falling perpendicularly on the emulsion. They found that the probability constant c_1 should be the same for thick and for thin emulsions and should equal $\pi\rho^2$ which is simply the chance of hitting a particular surface grain possessed by one of the N alpha-particles incident per cm^2. When an alpha-particle penetrates to a depth δ, the number of grains (k) made developable will be given by

$$(\pi\rho^2 \cdot \delta) \cdot G_0/\delta = k$$

whence

$$c_1 = \pi\rho^2 = k/G_0$$

(G_0 being the number of grains/cm^2 of emulsion surface). The photographic densities in their experiment did not exceed 3.5.

3. Commercial Emulsions—Noncollimated Alpha-Rays—High Densities

Further studies of the density law under wide variations of intensity, temperature, density and type of emulsion have been made by Sheppard, Wilkins, Wightman and Wolfe.[5] Their results may be summarized as follows.

(a) When an attempt is made to fit Eq. (1) to data of a *process* emulsion for exposure to a non-collimated alpha-ray source close to the film, where the exposures were prolonged until at least 99 percent of the grains had been affected, giving densities as high as 4.93, c_1 does not stay constant but decreases until for the largest densities c_1 is only about 10 percent of its value for low densities.

(b) In the case of a double-coated emulsion (portrait pan) with layers whose average grain size differed, c_1 instead of decreasing, rose through a maximum and then fell.

(c) At −185°C, the value of the exponential-constant fell to about one-third of its value at 20°C. This is accounted for not by a difference in range but by the number of grains per track.

(d) The density-exposure relation instead of being represented by the simple relation (1) where c_1 is a constant requires a second equation to take the variability of c_1 into account. The theoretical relations derived were

$$D = 1.57 D_{\max}(1 - e^{G/G_m}), \qquad (2)$$

$$G = G_m(1 - e^{-k(N/G_m)}), \qquad (3)$$

where G = number of grains "hit" by alpha-particles, G_m = number of grains in the emulsion within the range of the alpha-rays, N = number of alpha-rays, and k = average number of grains per track. G, G_m and N are all per sq. cm.

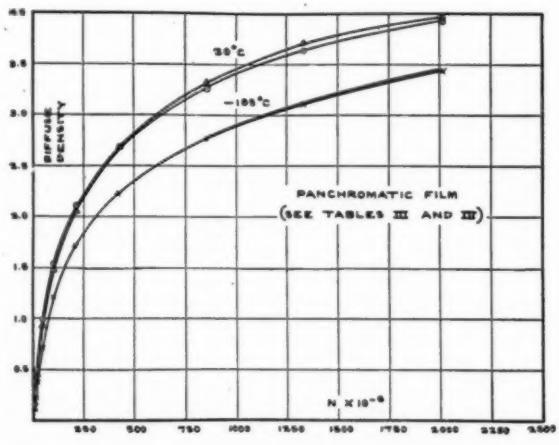


FIG. 2. Relation between density and number of alpha-particles.

Panchromatic Emulsion

$D_{m1} = 1.45$ $D_{m2} = 2.77$
$D_m = D_{m1} + D_{m2} = 4.22$ Fog = 0.50
$\overline{\pi r^2} = 0.611\mu^2$

The agreement between theory and observation is indicated in Figs. 1 and 2. If it is recalled that a density of 5 means that only 1/100,000

TABLE I.

	Weak Source Exposure Time between Exposure and Development	Density	Strong Source Exposure Average Time between Exposure and Development	Density
Film No. 15 A.*	22 hr. 50 min.	0.86	10 min.	0.86
B.	2 min.			
Film No. 17 A.	22 hr. 56 min.	0.85	22 hr. 52 min.	0.88
B.	8 min.		4 min.	0.80
Film No. 18 A.	46 hr. 19 min.	0.88	52 hr. 55 min.	0.91
B.	20 hr. 40 min.		33 hr. 33 min.	0.88
			5 min.	0.81
Film No. 19 A.	35 hr. 57 min.	0.83	47 hr. 54 min.	0.88
B.	10 hr. 18 min.		47 hr. 43 min.	0.88
			23 hr. 8 min.	0.86
			6 min.	0.79
Film No. 23 A.	36 hr.	0.78	43 hr. 11 min.	0.80
B.	10 hr. 21 min.		43 hr.	0.79
			23 hr. 10 min.	0.76
			17 min.	0.72
			7 min.	0.72

* A. Time between beginning of exposure and development.
B. Time between end of exposure and development.

of the light incident on it in the densitometer is transmitted by the plate and that for low densities the fog correction is of the order of 90 percent of the observed density, the difficulty of high precision in such measurements at the extreme density limits will be appreciated.

Validity of the Reciprocity Law

In Kinoshita's Eq. (1) and in the Eqs. (2) and (3) N represents the total number of alpha-rays falling on the emulsion. If the data for such an equation are all taken with the same source, the question arises as to the difference in density which might arise if a stronger source were used for a shorter time to produce the same number of particles. It is generally stated in the literature that "the same density is produced by the same number of alpha-particles per square centimeter of emulsion surface independent of the time of radiation." The first evidence for this was in Kinoshita's work[1] but this was for single grain layer emulsions and the intensity range ratio was only 6.5 to 1. H. Salbach[6] checked this reciprocity relation over a range of 7.3 to 1. Wolfe and Wilkins,[7] however, in extending the intensity ratio to 180 to 1, found an *apparent* departure from the reciprocity relation whose cause they traced to the effect of latent image growth* and to the recoil of active aggregates from the source to the emulsion. The error due to the recoil of active aggregates can be prevented by interposing a very thin foil between the source and the photographic emulsion. To understand how to correct for the latent image effect it is necessary to consider a typical experiment.

"A strong source exposure (film 17) was made at both the beginning and the end of the weak source exposure. The strong source gave a higher density when exposed 23 hours before development than when exposed immediately before development. The weak source density was intermediate between the strong source densities. This indicated that the reciprocity law held but that a growth of the latent photographic image might easily cause spurious effects which might be mistaken for failure of the reciprocity law."

TABLE II.

	Weak Source Density	Strong Source Density	$D_s - D_w$
Film No. 18	0.88	0.88	0.00
Film No. 19	.83	.86	+0.03
Film No. 23	.78	.76	−0.02

On Films 18, 19 and 23, the strong exposure was made when the weak exposure was half completed. Table I shows the data for these four exposures. The results of exposures 18, 19 and 23 in which the exposures were arranged to compensate for latent image growth are given in Table II.

* Such a growth for alpha-rays was reported by M. Blau, reference 8.

These differences are within experimental error and are much less than those produced for even smaller ratios in the case of light.

Photographic Counting of Alpha-Rays

We may therefore conclude:

(1) That alpha-rays may be counted photographically by Eqs. (2) and (3). These equations may be combined in the graph of Fig. 3 to save much time in calculation. For "process" emulsions at room temperature k/G_m seems to be equal to the average projected area of the grains; and D_m can be obtained from the manufacturer for the emulsion used. (If the range of the particles is greater than the thickness of the emulsion, D_m is the D_{max} of the emulsion. Otherwise the appropriate fraction must be used.)

(2) That if alpha-rays are to be counted by a photographic comparison of an unknown with a

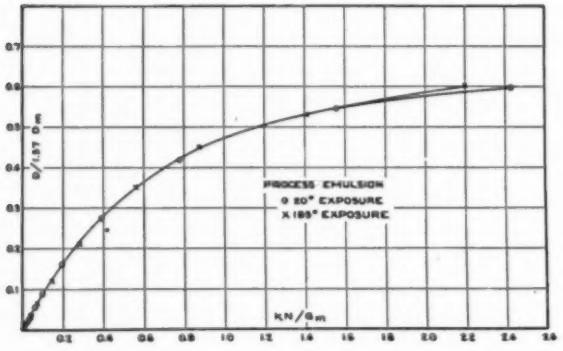


Fig. 3. Fraction of maximum density produced in terms of the number of alpha-rays and the emulsion characteristics.

standard source, then the reciprocity law can be safely used only if care is taken to avoid a latent image anomaly by allowing time between exposure and development equivalent to making the strong exposure midway in the longer (weak) exposure.

II. The Tracks of Individual Particles in Photographic Emulsions

To see the tracks of individual high energy atomic particles such as alpha-rays, protons or deuterons, the plates, after development, must be examined by a microscope. If one uses ordinary bright field illumination, it will be necessary to use rather coarse-grained emulsions. However, finer grained emulsions offer certain distinct advantages (some of which will be mentioned below). To see these fine grains the principle of the ultramicroscope is used, i.e., the grains are seen by scattered light. The microscope is fitted with a dark field condenser whose cone of light is arranged to come to a focus in the emulsion. The grains then appear as bright points of light on a dark background.

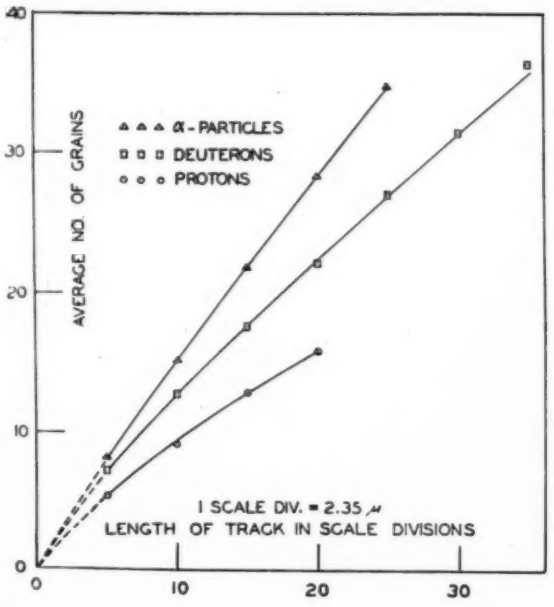


Fig. 4. Comparative spacing of alpha, deuteron and proton tracks in an Ilford R2 emulsion (Wilkins and St. Helens).

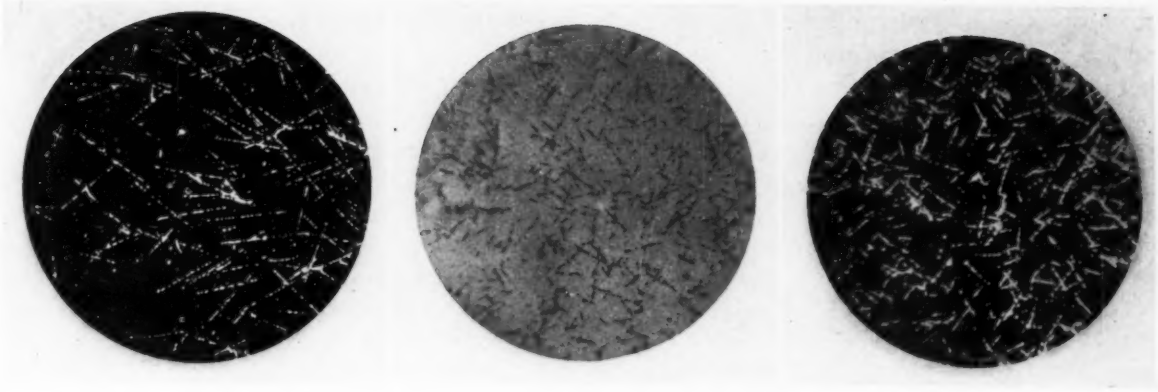
The Choice of Emulsion

The range of average grain-size over which an emulsion is sensitive to alpha-rays is larger than it is for protons.[9] One can therefore make emulsions sensitive to alpha-rays but not to protons by using an average grain diameter less than about 0.5μ or slightly greater than 1μ.

Some reasons for preferring fine-grained emulsions (and consequently darkfield illumination to make such fine grains visible) are as follows.

(1) The grains are not only much more numerous but also more uniform.

(2) Fine-grained emulsions can be made which give a sufficiently marked variation in grain-spacing for alpha-rays, deuterons and protons to



(a) (b) (c)

FIG. 5. (a) Dark field photomicrograph of emulsion EK-KL 3966. "Dark field stop" illumination. 8 mm objective—10× eyepiece. (b) Bright field photomicrograph of emulsion EK-KL 3966. (c) Dark field photomicrograph of Kodak emulsion 110812. (Reduction ⅓.)

serve as a basis for identification of tracks of unknown origin. Fig. 4 shows the result of a study of the response of an untreated Ilford R_2 emulsion to these three types of particles.[10]

(3) The grain-spacing, as can be seen from Fig. 4, tends to be less at the slow end of the track. This makes it possible to determine the direction of the particle.

(4) The sensitivity of fine-grained emulsions can be greatly increased by the use of sensitizers (see below).

A disadvantage is that "fog" due both to ordinary development-fog and to the grains made developable by the mechanical stresses produced in the gelatin by evacuating the "camera" containing the plates, gives a background which tends to obscure the tracks.

The making of suitable photographic emulsions will therefore involve (1) the selection of an emulsion of suitable grain size to give as many separately visible grains as possible, (2) the sensitization of this emulsion so as to record the full range of high energy protons, and (3) the treatment of the plate to reduce background fog to a minimum.

SENSITIZATION

An extremely important discovery due to M. Blau is that when certain emulsions are bathed in a solution of pinakryptol yellow (a *de*sensitizer in ordinary photographic processes) the tracks due to the passage of protons are greatly lengthened. An Ilford R_2 emulsion (Batch 625), for example, bathed 2 min. in 1 : 200 pinakryptol solution was found by Dr. G. Kuerti and the author to have proton tracks 8 or 9 times as long as an untreated plate. The sensitivity of the plate was so increased that the track corresponded with the full range of the proton in the emulsion.

FIG. 5(d). Tracks of protons in an Ilford R2 emulsion sensitized by bathing in a 1 : 200 solution of pinakryptal yellow. Mag. = 500 diam.

A difficulty with pinakryptol sensitization is that it is temporary. The cooperation of the Eastman Kodak Company was therefore enlisted, and in conjunction with Dr. E. E. Jelley of this company a considerable number of emulsions were tested. One was finally selected which possessed a high sensitivity to α-particles, protons and deuterons, and had satisfactory stability.

The photographs in Fig. 5 illustrate some of the points mentioned above. In (a) and (b) are

shown tracks of a large-grained emulsion in dark and bright field. Fig. 5(c) shows a dark field photomicrograph of a fine-grain emulsion whose grain size is about half that of 5(a). The long proton tracks obtained by sensitization by pinakryptol yellow are shown by Fig. 5(d).

Processing Technique

An ordinary Elon-hydroquinone developer such as the Kodak D11 Process Developer is satisfactory. Development for about 3 min. at 65°F (18°C) suffices to bring out the grains with a minimum of background fog. If a slower developer should be desired to allow of grain growth the more rapidly acting Elon may be omitted and a Special Hydroquinone developer used.

Table III.

	D11	Special
Water	500 cc	500 cc
Elon	1 g	
Sodium Sulphite	75 g	50 g
Hydroquinone	9 g	10 g
Sodium Carbonate	25 g	
Potassium Carbonate		50
Potassium Bromide	5 g	5 g
Water to make	1 liter	1 liter

Dissolve chemicals in the order given—use undiluted.

There is comparatively little difference in the developers suitable for such work. The sodium or potassium carbonate softens the gelatin to allow the developer to penetrate. The potassium bromide acts as a restrainer, prevents fog and increases contrast. The sodium sulphite prevents excessive oxidation of the developer by air.

After development, the plate is fixed in the standard acid Hardening Fixing Bath. Since these plates are to be examined microscopically some special precautions not necessary in ordinary photographic processing should be observed. To keep the fog to a minimum the less light of any kind used the better. Development should be in glass dishes. Most of the plastics (Tenite excepted) and even stainless steel give more fog than can be tolerated for this work. The deposit left from the wash in tap water may be largely removed by rinsing in a 1-percent acetic acid solution. The final rinse should be in distilled water.

Special care should be taken at every stage to see that the emulsion surface of the plate is not scratched (for example by laying the plate emulsion-side down to cut it) as such scratches show up in dark field examination.

Microscope Technique

When possible, it is a great advantage to cut the plates to standard microscope slide size (1×3 inches). The plates then fit the holder on the microscope stage and are firmly held in place. It is a great advantage, too, to have the microscope fitted with a mechanical stage so that the coordinates of any tracks of interest can be noted and the point found again.

Dark field illumination may be secured in several ways. A dark field condenser (paraboloid or cardioid) can be used to replace the usual Abbé condenser, or a "dark field element" to replace the top element of a divisible Abbé condenser, or thirdly, most microscopes are fitted with substage condensers which have an iris diaphragm below the condenser with a slotted ring into which the dark field stop, ground-glass or blue glass furnished with the microscope may be slipped. Fine dark field illumination with such a stop or a "dark field element" is secured by using an 8-mm (21X) objective and varying the illumination by varying the iris diaphragm and the distance of the condenser below the plate. The centering of the optical system and the numerical aperture of the objective are, however, very important.* For higher magnifications a cardioid or paraboloid condenser is used. Oil must then be used between the condenser and the glass side of the plate to be examined.**

In using dark field illumination it is important that the apex of the cone of light is located in the emulsion. This limits the thickness of the plates which can be used with fixed working-distance paraboloid and cardioid condensers.

* Objectives fitted with variable diaphragms are available. Brass washers come in a size to slip into most 8-mm separable objectives. A set of these counter-bored to various diameters gives a simple means of cutting down the aperture.

** Cedar oil gums and is not to be recommended. Castor oil is preferable.

Length of Tracks in Emulsions—Thickness of Emulsions

The stopping power of these emulsions for alpha-rays is about 1380. Thus the range of a 7.7-Mev RaC′ alpha-ray (air range 6.97 cm) is about 50.5 microns. The range of 7-Mev protons is about 60 cm in air. Tracks of 7-Mev protons scattered by a thin platinum foil (0.2 mil) at 40° were found as long as 375 microns in the Kodak emulsion with single coating. The approximate equivalence of the ratios[11] suggests that the whole range of the protons was being recorded in this emulsion.

The standard commercial coating thickness of emulsions of this type is only about 20 microns. It is thus evident that if RaC′ alpha-rays were to strike the emulsion perpendicularly, less than half the complete track would be recorded.* This must be taken into account in the design of apparatus. For example, in the scattering camera, described later, the particles strike the plate at a glancing angle (4 degrees) so that even 7-Mev protons are wholly recorded.

Stereoscopic Photomicrographs

In cases where it is necessary to measure the absolute lengths of tracks or the angles between tracks, stereoscopic pictures may be taken. In general, there are two systems, one involving angular motion and the other a linear displacement. The formula for a tilting stage method has been given by Myssowsky and Tschijow,[12] and by Jdanoff.[9] The conditions for orthostereoscopic photomicrographs using a linear displacement and a diaphragm whose size and position in the tube of the microscope are specified, have been examined by Martin and Wilkins.[13] A special stereoscope of the Wheatstone type was developed by these latter authors which makes it possible to measure directly the lengths and angles of a true-scale reconstruction of the original tracks.

Some Typical Applications

1. Radiographs

If a section of a radioactive mineral is laid for a while on a photographic plate the veins carrying the radioactive matter are sharply outlined in the developed plate. Fig. 6 shows a vein of unusually rich pitchblende interlaced with fine threads of visible silver which show up well in a high contrast (fine-grained) process emulsion.

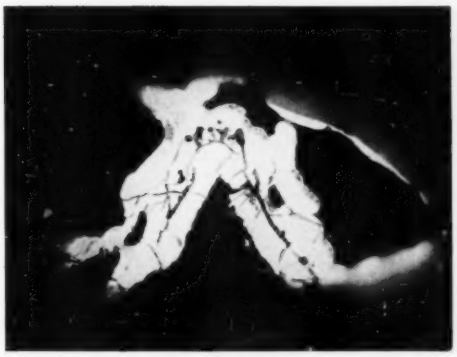


Fig. 6. Radiograph of a rich specimen of Great Bear Lake pitchblende interlaced with seams of silver. (Process emulsion.)

2. Radiocolloid Aggregates

Not so well known is the use of the photographic emulsion to study the nature of the distribution of radioactive elements in solution. Some years ago Paneth showed by dialysis that in an aqueous solution of lead nitrate (in which in addition to ordinary lead there was the lead isotope RaD and its decay products RaE and polonium) the lead was held in a molecularly disperse solution whereas the RaE and the polonium behaved like colloids—i.e., they formed aggregates. Mlle. Chamie[14] detected these aggregates by placing some drops of a radioactive solution on a photographic plate. A great deal has been learned concerning colloids and the degree of solubility of various elements from a continuation of these studies.[15] For example, Fig. 7 shows the effect of acidity on the aggregation of thorium C.[16] The exposure in this case was made by placing a drop of the solution on a very thin foil of mica which covered the photographic plate.* There are still many points in dispute concerning quantitative measurements on these radiocolloid aggregates. For example, does the size of the aggregate vary with depth in the solution? This has been reported but not confirmed.[15] The writer in repeating Mlle.

* Double-coated emulsions can be made but emulsions still thicker tend to strip off in a vacuum. Double-coated emulsions may look milky even after lengthy fixing. This is probably due to the large number of holes left after development. The plates clear as they dry.

* Very acid solutions cannot be put directly on a photographic emulsion as the emulsion dissolves.

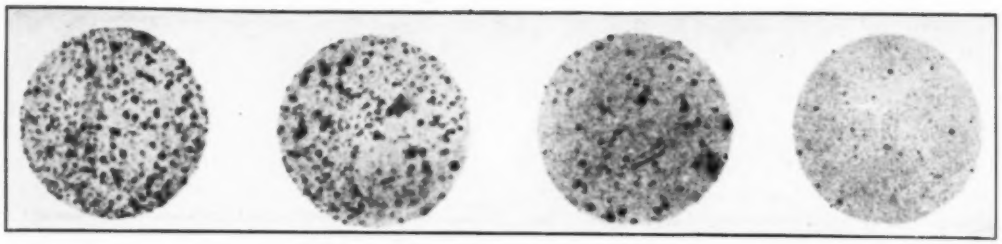


FIG. 7. Effect of acidity on aggregation of thorium C (Hahn and Werner).

Chamie's experiment with the new Kodak fine-grained emulsion has recently secured some beautiful examples of the presence of these aggregates in a radium solution which suggest a possible technique for estimating the quantity of radioactive material in the colloid aggregate. Figs. 8 and 9 show bright-field and dark-field photomicrographs. The outer radius corresponds with the range of the RaC′ alpha-particle (50.5 microns). The radius of the central dark kernel is variable but this variability is not due to the aggregate being formed on a sizable, nonradioactive particle. A comparison of the bright and dark field photographs shows that whereas the dark tracks of the bright field picture become bright tracks in the dark field picture, the core remains black in each but it differs in size. This is due to the fact that so many grains have been made developable that the thick mat of silver no longer scatters light in the dark field. The size of the dark area is thus a measure of the number of alpha-rays emitted and if the decay constant controlling the emission and the time of exposure are known, the amount of radioactive material in these radiocolloid aggregates can be calculated. The calibration is done in terms of a faint halo in which the number of alpha-rays can be counted.*

3. Counting of Alpha-Rays and Protons

The use of the density relation for the photographic counting of alpha-rays has already been described in detail above. For weak sources individual tracks can be counted.

* If the size of these colloid aggregates varies with depth and can be thus measured, an interesting variant of the Perrin experiment for the determination of the Avogadro number is possible.

4. The Determination of Half-Lives of Radioactive Elements

If the emulsion is moved at a known rate relative to the source the half-life of a radioactive element can be measured. Over the range for which the density can be taken as proportional to the number of particles hitting the emulsion, a graph of density *vs.* time on semi-log paper will be linear and the half-life can be read directly from the graph. It is interesting to note that such a determination is not confined to

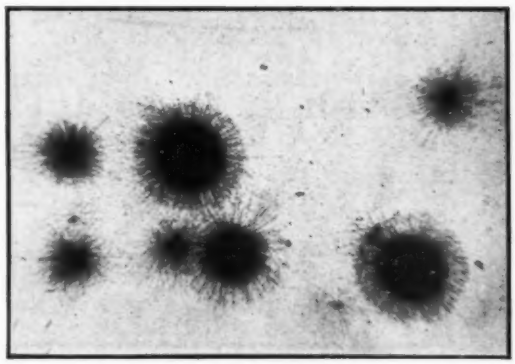


FIG. 8. Bright field photomicrograph of radiocolloid aggregates. (Kodak Experimental Emulsion 110069. Diam. of halos 50μ.)

alpha-emitters. Wilkins and Burdick[17] developed the method for the study of thorium B—a β-emitter which controlled the decay of the products ThC and ThC′ whose alpha-rays were mainly instrumental in affecting the plate. The method has also been applied to artificially activated electron emitters of suitable period.

5. Radium Infected Plates

If a plate is soaked in a neutral weak solution of radium (about 10^{-8} g/cc) and left for some

days, the successive alpha-rays emitted as the radium changes to lead leave tracks radiating from a point in the emulsion and give visible proof of the existence of the several generations of atoms from a single parent. Such a star is shown in Fig. 10.

6. Nuclear Reactions in Impregnated Plates

A number of elements such as boron, lithium, zinc, uranium etc., can be directly incorporated in a photographic emulsion without causing excessive fogging. H. J. Taylor and M. Goldhaber[18] used this technique for the study of the disintegration of boron and lithium by neutrons. They based their technique on the fact that they found the Ilford R1 plate sensitive to alpha-rays

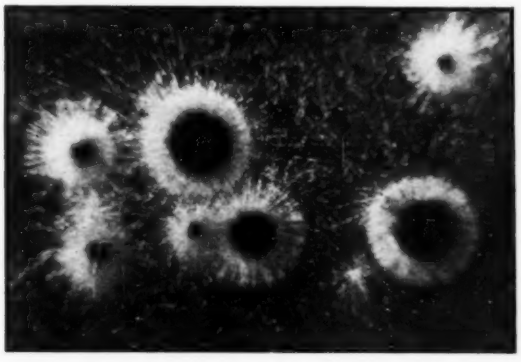


Fig. 9. Dark field photomicrograph of radiocolloid aggregates. (Kodak Experimental Emulsion 110069. Diam. of halos 50μ.)

but not to protons. Short tracks in the emulsions could then be attributed to alpha-rays produced in the reactions

$$B^{10}+n^1 \rightarrow Li^7+He^4,$$
$$Li^6+n^1 \rightarrow He^4+H^3.$$

In a suitable emulsion, the latter yields a beautiful pair of tracks.

7. The Detection of Fission

The study of the recently discovered fission of the uranium atom should also be detectable by the emulsion method. The track would be very short as the air range of the fission particle is little more than a centimeter and the large nuclear charge of this particle might lead to bad "scattering." L. Myssowsky and A. Jdanoff[19] have reported a track which they interpret as due to this fission. The difference in response of an emulsion to alpha-rays and protons suggests that an emulsion with quite different grain character may prove more suitable for these heavy, highly charged fission particles.

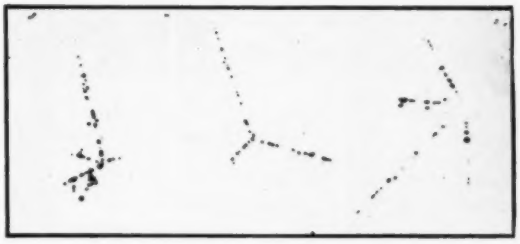


Fig. 10. Successive steps in the disintegration of single radium atoms as they change to lead. The photographs were made by placing a drop of water containing some radium on a photographic plate. After some weeks the plate was developed and examined in the microscope (magnification 900). The three pictures correspond to examples in which three, four and the whole five steps in the disintegration had occurred at the time the plate was developed. The long track is RaC′ (50μ).

8. Cosmic Rays

The emulsion technique has proved of great interest in the study of cosmic rays. In an unsensitized Ilford R2 emulsion carried in the National Geographic-U. S. Army Stratosphere Balloon in 1935 Wilkins and St. Helens[20] found tracks of many high energy alpha-rays and protons—the energy of one alpha-track being estimated at 100 million electron volts. They also reported a "burst" consisting of a dozen proton tracks radiating from a point. They later found these bursts to be quite common in plates left exposed for some time on Mt. Evans (14,500 ft.). M. Blau[21] has photographed a burst of five protons and alpha-rays originating in an emulsion exposed at high altitude, and Fig. 11 shows a "burst" of a hundred atomic particles photographed by Jdanoff.[22] It is possible that some elements are more susceptible to multiple disintegration by cosmic rays than others. This can well be studied further by this technique. H. J. Taylor reports that samarium seems to be an example.

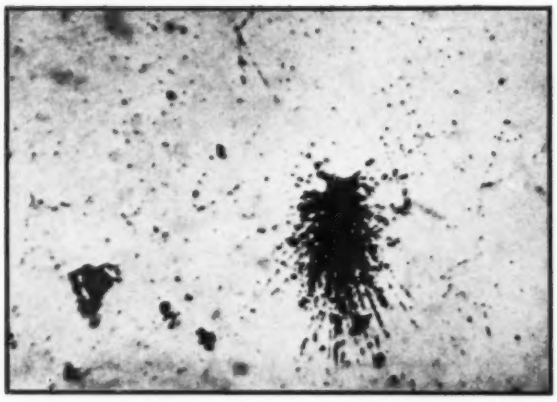


FIG. 11. Burst of 100 protons originating in an emulsion exposed to cosmic rays at high altitude (Jdanoff).

9. NUCLEAR SCATTERING

One of the latest applications of the emulsion technique is in the camera recently developed for the study of nuclear scattering. The camera can be attached to a cyclotron (Fig. 12). The intense beam of particles is then scattered as the particles come near the nuclei in a thin foil at the center of the camera. Such of the scattered particles as pass through small pin-holes in the surrounding ring then leave their tracks in the photographic plates distributed around the camera. The numbers and lengths of the tracks can be counted and their nature identified—the latter being an especially important point since disintegration is often superimposed on scattering. Much new information has already been found by this method.

10. IDENTIFICATION OF RADIOACTIVE ISOTOPES

There are cases in which some one isotope of an element may be radioactive. If the isotopes are separated by a mass spectrograph and deposited on a suitable plate, the isotopic deposits can be examined separately for tracks. This has been done in the case of samarium.[23] Several months were left between the laying down of the deposit and development. In this interval the decay of the samarium was registered. This is probably one of the best examples of the delicacy of the emulsion technique as the half-life of samarium is so extremely long (10^{12} years) that the decay of a very few atoms had to serve for the identification.[24]

These are but a few of the applications of these particle-sensitive emulsions. Many others are obvious. The radiochemist is provided with a tool to identify and measure the activity of the alpha-ray elements in precipates and solutions which is of the greatest help in step-by-step checking of his separations. If the radon and thoron in a mineral can be collected, the relative numbers of the easily identifiable RaC′ and ThC′ tracks give an easy determination of the relative proportion of the radium and thorium present. Numerous applications in the further study of solutions and crystallization along the lines suggested in Hahn's *Radiochemistry* and in the examination of nuclear disintegrations will doubtless occur for the photographic emulsion supplies a device which for atomic particles is equivalent to a Wilson cloud chamber on one-thousandth the scale and which has the advantage of simplicity, of continuous registration, and of differentiated response to various particles. The possibilities of the use of the standard non-sensitized emulsion along with the emulsion sensitized to protons should be kept in mind.*

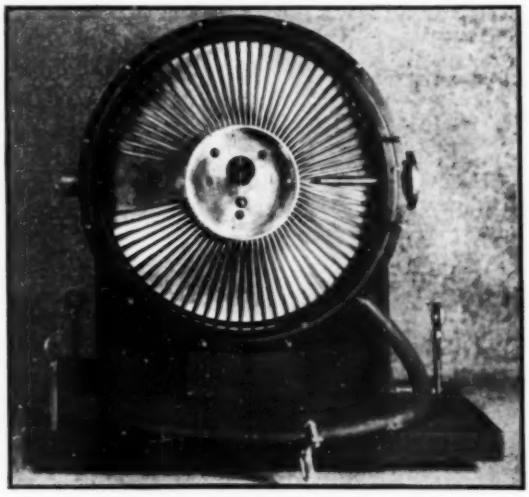


FIG. 12. Camera for the study of nuclear scattering (Wilkins and Kuerti).

* These two emulsions are available from the Eastman Kodak Company. Kodak Alpha Ray Plate—sensitive to alpha-rays. Kodak Proton Plate—sensitized to respond to protons. The latter, therefore, records alpha-rays, protons and deuterons.

Bibliography

1. S. Kinoshita, Proc. Roy. Soc. **A83**, 432–53 (1909–10).
2. T. Svedberg and H. Andersson, J. Phot. **61**, 325–32 (1921).
3. J. Eggert and F. Luft, Zeits. f. physik. Chemie (Bodenstein Festband), Erganzungsband, 745–754 (1931).
4. T. R. Wilkins and R. N. Wolfe, J. Opt. Soc. Am. **23**, 324–332 (1933).
5. S. E. Sheppard, T. R. Wilkins, E. P. Wightman and R. N. Wolfe, J. Frank. Inst. **222**, 417–460 (1936).
6. H. Sallbach, Zeits. f. Physik **11**, 107–128 (1922).
7. R. N. Wolfe and T. R. Wilkins, J. Opt. Soc. Am. **26**, 105–110 (1936).
8. M. Blau, Akad. Wiss. Wien. (IIA) **140**, 623–628 (1931).
9. A. Jdanoff, J. de phys. et rad. **6**, 223–241 (1935).
10. T. R. Wilkins and H. J. St. Helens, Phys. Rev. **54**, 783–788 (1938).
11. H. A. Bethe and M. S. Livingston, Rev. Mod. Phys. **9**, 245 (1937).
12. L. Myssowsky and P. Tschijow, Zeits. f. Physik **44**, 408 (1927).
13. L. C. Martin and T. R. Wilkins, J. Opt. Soc. Am. **27**, 340–349 (1937).
14. Mlle. C. Chamie, Comptes rendus (1929–31). See also O. Hahn, reference 15.
15. O. Hahn, *Applied Radiochemistry* (Cornell University Press, 1936).
16. O. Hahn and O. Werner, reference 15.
17. T. R. Wilkins and S. D. Burdick, Master's Thesis, University of Rochester, 1933.
18. H. J. Taylor, Proc. Phys. Soc. **47**, 873–876 (1935); W. E. Burcham and M. Goldhaber, Proc. Camb. Phil. Soc. **32**, 632–636 (1936).
19. A. Jdanoff and L. Myssowsky, Nature **143**, 795 (1939).
20. T. R. Wilkins, National Geog. Soc., Stratosphere Series **2** (1937).
21. M. Blau, Nature **140**, 585 (1937); M. Blau and H. Wambacher, Akad. Wiss. Wien, Ber. **146**, 2a. 7–8, pp. 469–477 (1937); Ber. 146. 2a. 9–10, pp. 623–641 (1937).
22. A. Jdanoff, Nature **143**, 682 (1939).
23. T. R. Wilkins and A. J. Dempster, Phys. Rev. **54**, 315(A) (1938).
24. C. F. Powell and G. E. F. Fertel in a letter to *Nature* (**144**, 115 (1939)) appearing after this article was sent in, call attention to their studies of the tracks of protons resulting from the bombardment of boron by deuterons. The Scattering Camera is an extension and refinement of this technique in that the angular distribution of the reaction is studied simultaneously with the study of the energies of the proton groups. The results of such studies will be reported shortly. The authors quite rightly pay tribute to the great value of the emulsion technique.

Physics in Color Photography

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MODERN color photography is a triumph of applied chemistry. The fact that the science of physics has had no part in the recent spectacular improvements is amazing to those who remember that the basic idea of three-color photography was conceived by the physicist Maxwell[1] as a result of physical measurements made during his study of color vision. The abandonment by physicists of active interest in color photography can be traced to events which, in the light of recent discoveries, can now be re-evaluated with the hope of renewing the creative activity of physicists in the fascinating science of color reproduction.

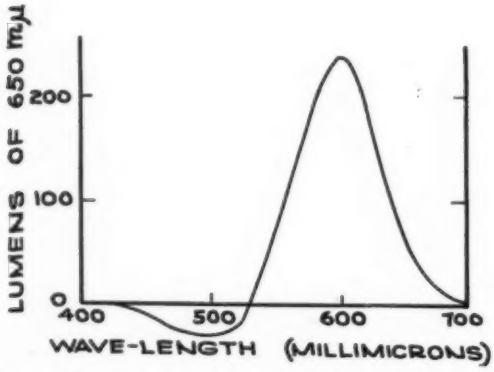

FIG. 1. Color-mixture for red unitary color, showing lumens of 650 mμ light required in a mixture with 425 mμ and 530 mμ to match one watt of each indicated wave-length.

Maxwell's investigations of the nature of color vision[2] led him to conclude that the visual appearance of any color could be duplicated by the mixture of suitable intensities of the light from three differently colored sources. These basic colors from which colors are synthesized will be called unitary colors, throughout this paper. Maxwell experienced some difficulty in matching, that is, duplicating the visual appearance of some of the most saturated colors, but believed that if sufficiently saturated unitary colors were used, all colors could be matched. Some later authors have assumed that only one set of such colors could be used successfully to synthesize all colors. These authors have frequently attributed profound physiological or psychological significance to their special sets of unitary colors, calling them primary colors. Such limitation to one set of unitary colors for use in color syntheses cannot be justified by experiments of the type performed by Maxwell. More recent investigations have revealed that no set of three colors can be employed which will fully duplicate the saturation of all the most saturated colors. This fact does not nullify the usefulness of Maxwell's discovery because such highly saturated colors are rarely if ever encountered, especially by the photographer. The visual appearance of the greatest variety of colors can be matched if highly saturated red, green, and blue colors are used for the synthesis. For this reason alone, three-color photography is based on the use of these unitary colors. Subsequent discussion will show that the employment of cyan (blue-green), magenta, and yellow dyes or pigments in "subtractive" color reproduction is optically equivalent to using these red, green, and blue unitary colors.

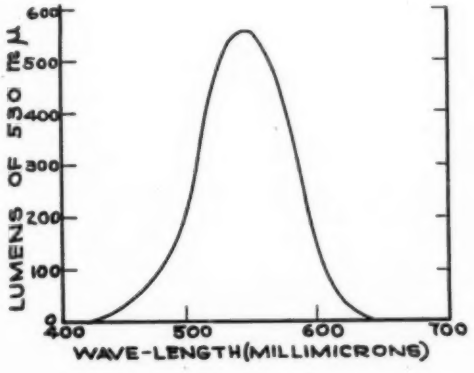

FIG. 2. Color-mixture curve for green unitary color, showing lumens of 530 mμ light required in a mixture with 425 mμ and 650 mμ to match one watt of each indicated wave-length.

Maxwell determined the relative brightnesses of his unitary colors required for a mixture that would visually match the color of a standard intensity of energy from each region of the spectrum. The results of similar measurements are shown by the color-mixture curves in Figs. 1, 2, and 3. Although these curves were derived from measurements of spectrum colors, such colors are rarely encountered by photographers. Consequently, the following interpretation of the curves will be given in terms of the type of colors encountered almost invariably in photography. Almost every color occurring in nature and in art consists of a mixture of all or almost all of the wave-lengths of the spectrum. The intensities of the various wave-lengths present in any particular color can be represented by the heights of the points on a spectral-distribution curve, such as that shown in Fig. 4. Maxwell and his successors proved experimentally that the visual appearance of such a mixed color can be matched by a combination of the unitary colors having brightnesses that can be determined by calculations employing the data shown in Figs. 1, 2,

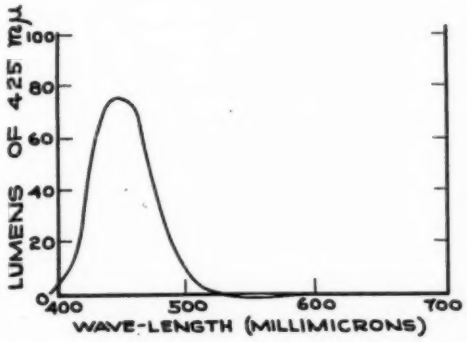

FIG. 3. Color-mixture curve for blue unitary color, showing lumens of 425 mμ light required in a mixture with 530 mμ and 650 mμ to match one watt of each indicated wave-length.

and 3. The intensity shown by the height of each point on the curve in Fig. 4 should be multiplied by the brightness of the red unitary color required to match unit intensity of energy at the corresponding wave-length, shown by the height of the curve in Fig. 1. When the heights of the points at corresponding wave-lengths in Figs. 1 and 4 have been multiplied, the results can be represented in a curve such as that shown in Fig. 5. The area enclosed between the horizontal axis and the portions of the curve in Fig. 5 appearing below the axis should be measured and subtracted from the area enclosed between the horizontal axis and the portions of the curve appearing above the axis. The net area resulting from this calculation is the brightness of the red unitary color that should be used in the mixture to match the sample color. The heights of corresponding points in Figs. 4 and 2 should be multiplied to give the heights of the points on the curve shown in Fig. 6. The net area between this curve and the horizontal axis is the brightness of the green unitary color that should be used in the mixture to match the sample. Finally, the heights of corresponding points in Figs. 4 and 3 should be multiplied to give the heights of the points on the curve in Fig. 7. The net area between this curve and the horizontal axis is the brightness of the blue unitary color that should be used in the mixture to match the color of the sample. Frequently, colors having entirely different origins, such as natural flesh tint and a cosmetic preparation, will look exactly alike and yet have entirely different spectral-distribution curves. Nevertheless, the brightnesses of the unitary colors computed from the curves will be the same for all such samples. Whenever identical brightnesses result from such calculations, the colors for which they were calculated are perfectly matched, although marked differences may be indicated by their spectral-distribution curves. The color-mixture curves shown in Figs. 1, 2, and 3 are the only curves that can result in the determination

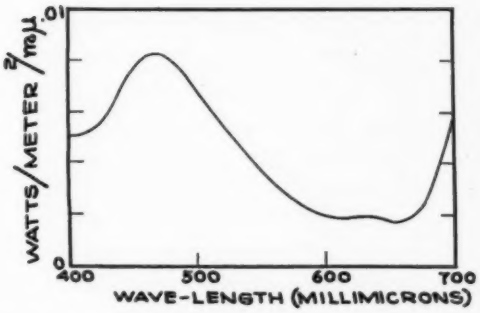

FIG. 4. Spectral distribution of energy from a green color stimulus, showing watts per square meter of area of stimulus per millimicron wave-length interval. The brightness of a surface diffusely radiating energy at the rate shown by this curve is 8.9 candles per square centimeter, or 28 millilamberts.

of the correct brightnesses of the corresponding unitary colors. If any other set of unitary colors is used each of the corresponding color-mixture curves[3] is the sum of suitable fractions of the three curves shown in Figs. 1, 2, and 3. Curves derived in this manner are called linear combinations of the original curves. If curves differing from linear combinations of the curves in Figs. 1, 2, and 3 are used for the determination of the brightnesses of any set of unitary colors,

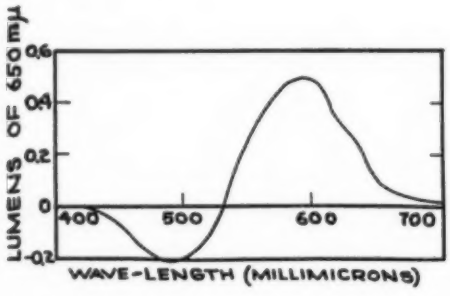

FIG. 5. Curve showing the products of the values given at corresponding wave-lengths by Figs. 1 and 4. Ordinates are lumens of 650 mμ per square meter per millimicron wave-length interval. The net area under this curve gives the brightness (lumens per square meter) of the 650 mμ unitary color necessary for the mixture matching the stimulus. This procedure gives 35 lumens per square meter (3.5 millilamberts) as the brightness of the 650 mμ unitary color necessary for the mixture matching the stimulus specified by Fig. 4.

then three errors will vitiate the results as follows:

1. Some or all colors will be incorrectly matched by the mixture of the computed brightnesses of the unitary colors.

2. Some or all sets of matched colors will be matched by sets of differing mixtures.

3. Some sets of visually dissimilar colors will be matched as visually identical colors.

Several modifications[4] of the procedure for calculating the brightnesses of the unitary colors have been devised in order to minimize the labor of calculation, but all the satisfactory methods are mathematically equivalent to the method just described and give identical results.

Maxwell's conception of three-color photography was based on his tacit assumption that the photographic plate responds to mixtures of colors in a manner such that it automatically performs all the essential operations of the calculations described above. Ives,[5] who was the leading exponent of Maxwell's idea, proposed that a color filter be placed somewhere in the path of the light in order to modify the effective sensitivity of the photographic plate to different wave-lengths so that the sensitivity will be as nearly as possible proportional to the heights of the points on a color-mixture curve such as that shown in Fig. 3. If the photographic plate integrates all the constituents of mixed colors in the manner assumed by Maxwell and Ives, then the transmittance of every point in a positive transparency made from such a plate will be proportional to the brightness of the blue unitary color required for the three-color mixtures matching the colors photographed. If transparencies are made from plates having effective spectral sensitivities proportional to the green and red color-mixture curves (for example, Figs. 2 and 1), then these transparencies will have transmittances proportional, respectively, to the brightnesses of the green and the red unitary colors required for the three-color mixtures matching the colors photographed. If images of these three transparencies are projected with light sources having the corresponding unitary colors, the colors synthesized in the superimposed images will automatically match all the colors originally photographed. The color-mixture curves which should be used are those which correspond to the unitary colors that are to be used in synthesizing the reproduction. All color-mixture curves for attainable unitary colors exhibit negative portions, as is evident in Fig. 1. Spectral sensitivities which are less than zero in some parts of the spectrum are of course unobtainable, although Hardy and Wurzburg[6] have recently suggested methods for obtaining the effects of such negative spectral sensitivities. The use of photographic filter and plate combinations such that the effective spectral sensitivity of each combination is proportional to the positive portions of the corresponding color-mixture curve, having zero sensitivity wherever the color-mixture curve passes below the zero axis, results in the most accurate practical approximation to the theoretically correct sensitivities.[7]

The foregoing is an outline of the additive process conceived by Maxwell. The subtractive process, which is the most convenient and frequently used method of color reproduction, is

simply a substitute for the clumsy triple-projection method. Errors in the reproduction by triple projection that would be caused by the use of materials having incorrect spectral sensitivities are still present in the subtractive method of reproduction. Imperfections peculiar to this method introduce further errors, and these cannot be made to compensate for the errors arising from incorrect spectral sensitivity. For instance, it is obvious that if several colors having identical appearance but differing in spectral distribution produce differing densities on one or more of the photographic negatives, which would result from the failure to make the spectral sensitivities proportional to color-mixture curves, then the reproductions of these visually identical colors secured by any method of synthesis would differ among themselves. Therefore, some or all of these reproductions would necessarily differ from the original colors, as a direct consequence of the use of incorrect spectral sensitivities.

The failure to recognize the general applicability of color-mixture data led to early and very persistent lack of confidence in the suggestion that the spectral sensitivities for color photography should be identical with the color-mixture curves. It has been claimed that such spectral

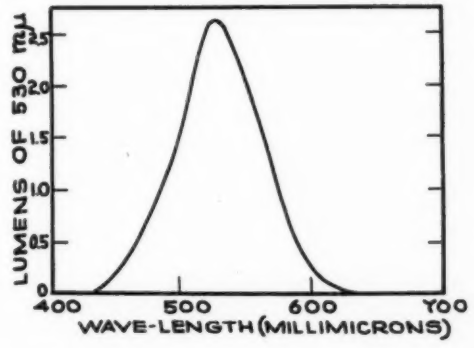

FIG. 6. Curve showing the products of the values given at corresponding wave-lengths by Figs. 2 and 4. Ordinates are lumens of 530 mμ per square meter per millimicron wave-length interval. The net area under this curve gives the brightness (lumens per square meter) of the 530 mμ unitary color necessary for the mixture matching the stimulus. The result is 21.3 millilamberts.

sensitivities are satisfactory only for the reproduction of the colors of the spectrum, and that their usefulness for the reproduction of less saturated colors has not and cannot be proved. This discussion of the significance of the color-

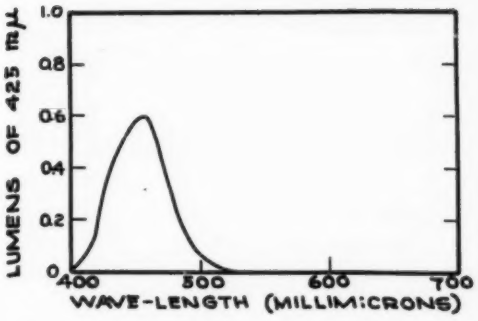

FIG. 7. Curve showing the products of the values given at corresponding wave-lengths of Figs. 3 and 4. Ordinates are lumens of 425 mμ per square meter per millimicron wave-length interval. The net area under this curve gives the brightness (lumens per square meter) of the 425 mμ unitary color necessary for the mixture matching the stimulus. The result is 3.2 millilamberts.

mixture curves emphasizes the fact that their usefulness is not confined to the matching of spectrum colors. It is obvious that if the photographic plate actually does integrate all the constituents of mixed colors, a behavior exactly equivalent to the calculations described above, then the accurate additive or subtractive photographic reproduction of all colors can be accomplished only by fulfilling the sensitivity requirements described in the preceding discussion. Any departures of the spectral sensitivities from the appropriate color-mixture curves will result in the errors previously mentioned.

Maxwell and Ives tacitly assumed that every wave-length present in the colors being photographed would contribute to the effective exposure of the photographic plate in proportion to the product of the intensity of that wave-length and the corresponding sensitivity of the plate. The assumption that all contributions to the exposure are effective, including those from wave-length regions which alone would be too weak to result in developable density, was first challenged in the early years of this century.[8] At that time several authors assumed that none of the constituent colors which alone would be ineffective could contribute any part of the effective exposure to mixed colors. The generally accepted criticism of all spectral sensitivities, that are proportional to either color-mixture curves or luminosity curves,[9] was based on this assumption which apparently originated from a misinterpretation of wedge spectrograms.[10] Most

discussions of the characteristics of filters for three-color photography accept as desirable the overlapping bands of uniform sensitivity which were derived from this assumption of the failure of photographic plates to accumulate the contributions of all wave-lengths. The apparent proof of the impossibility of applying physical color-mixture data to color photography was primarily responsible for the abandonment by physicists of almost all active interest in color reproduction.

Recently, however, three experimental investigations have been published which appear to justify a reconsideration of this subject. Van Kreveld[11] investigated the general response of photographic plates to mixtures of colors and found that, except for a minor, avoidable failure[12] due to the variation of contrast with wave-length, photographic plates do accumulate the contributions of all the constituents of mixed colors, no matter how feeble, in exactly the manner tacitly assumed by Maxwell and Ives. Webb[13] repeated van Kreveld's investigation with modifications, and confirmed this conclusion. Van Kreveld and Webb proved that if, for instance, the energy of each of five wave-lengths necessary to produce a density of 0.5 is determined for any photographic emulsion, then the mixture of all five wave-lengths consisting of one-fifth of each of these energies will also produce a density of 0.5. One-fifth of the energy necessary to produce a density of 0.5 is insufficient to produce appreciable density. The experiment described is therefore a decisive test between the assumptions of Ives and his critics. The assumption that when each of the constituents of a mixture is too weak to produce appreciable density the mixture itself cannot be photographically effective is proved false by the experiment.

Spencer[14] constructed a device for illuminating a test chart of colored papers with any specified spectral distribution of energy. By adjusting the distribution of energy provided by this illuminator so that it was proportional to the ratio of any theoretical spectral sensitivity to the actual spectral sensitivity of the emulsion used in the experiments, photographs were taken using a large variety of spectral sensitivities called for by the various theories of color reproduction. Unfortunately, the effects of the various sensitivities were not isolated from the imperfections of existing subtractive printing materials. Furthermore, the tests purporting to represent the use of color-mixture curves used curves corresponding to unattainably saturated unitary colors. This failure to use color-mixture curves corresponding to the unitary colors actually used in the reproduction resulted in more seriously degraded saturation reproduction than would have been obtained if such curves had been used.[7] However, the general results of Spencer's experiments indicate that the most satisfactory reproductions were obtained when the effective spectral sensitivities most closely resembled the proper color-mixture curves. For instance, Spencer concludes: "Provisionally it would appear that the failure of modern filters in their attempt to comply exactly with Bull's original specifications, renders them actually more suitable for three-colour subtractive photography than such 'ideal' filters." In another place he says that ". . . greater saturation is obtained by sloping off the filter record on either side rather than by extending the transmission evenly as has previously been proposed. Providing properly exposed negatives are made with such filters, the anomalous colour rendering due to this graded absorption predicted by previous workers is negligible in continuous-tone subtractive printing with modern emulsions." In view of the fact that commercial filters having the graded absorptions mentioned by Spencer give effective spectral sensitivities more nearly resembling color-mixture curves than they resemble overlapping bands of uniform sensitivity, the results of Spencer quoted above indicate that the closer approach to color-mixture curves results in superior color reproduction. Quite close approximations to the positive portions of color-mixture curves corresponding to practical unitary colors are now possible with commercially available filters, and the reproduction secured with the use of such filters is definitely superior to that secured with the use of the standard commercial filters mentioned by Spencer.

This review of the problem of the correct spectral sensitivities for color-separation records can be concluded with the assurance that the intuitions of Maxwell and Ives, so long distrusted by color photographers, have been completely

justified by the experimental investigations of van Kreveld and of Webb; that the application of color-mixture curves to color photography which was advocated by Ives received unexpected support in the investigations of Spencer; and that consequently the peculiarity of the photographic response which appeared to forbid the application of physical reasoning to color photography is a thirty-five-year-old misconception which need no longer discourage the interest of physicists in color photography.

The investigation of the subtractive method for synthesizing color reproductions is of especial interest to physicists. This method has been used empirically for many years and is of such great practical importance that a detailed study of its optical possibilities and limitations has become desirable. The details of such a study[15, 16] are so complicated that a complete discussion would be out of place in this paper. However, an outline of the reasoning can be presented in terms of a simplified example which will indicate the importance of the application of physical reasoning to subtractive color photography.

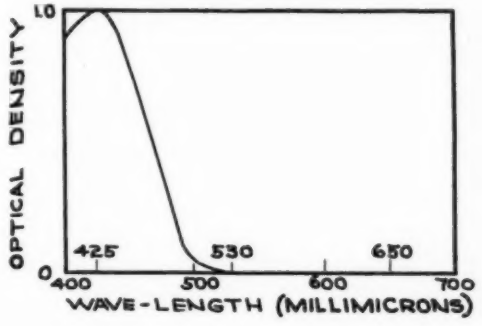

FIG. 8. Spectral density curves for a typical yellow dye.

Let us suppose that the unitary colors used to project the superimposed images of the three correctly prepared transparencies are pure spectral colors, for instance, those having wavelengths 425 mμ, 530 mμ, and 650 mμ. The transparencies customarily used for such triple projection consist of gray photographic deposits of varying density. If, however, the gray deposit in the transparency projected with the blue (425 mμ) light is converted into a yellow deposit which does not absorb either the green (530 mμ) or the red (650 mμ) light, but does absorb at every point the same percentage of the blue light as the gray deposit, then the reproduction secured by the substitution of this yellow transparency will be exactly the same as would result if the original gray deposit were projected with the others. Similarly, if the gray transparency used in the green projector can be converted into a magenta transparency which does not absorb either the blue (425 mμ) or the red (650 mμ) light, and if every point in the magenta deposit absorbs the same percentage of the green light as did the corresponding point in the gray deposit, the reproduction by triple projection will not exhibit any change. Finally, if the gray transparency used in the red projector can be converted into a cyan (bluish-green) transparency which does not absorb any blue (425 mμ) or green (530 mμ) light, but absorbs red light to the same extent as did the gray deposit, then again the reproduction by triple projection will remain unchanged. These three colored transparencies differ from the gray originals however, inasmuch as they can be superimposed and projected with a single lens. If a light source that radiates a white mixture of the three spectral colors is used, the resulting reproduction will be exactly the same as that secured by the triple projection of the three original gray transparencies. Each of the superimposed colored transparencies absorbs one and only one of the unitary colors in exactly the same manner as each of the gray transparencies absorbed only the one unitary color with which it was projected. If the original transparencies were prepared from photographic plates having corrected spectral sensitivities proportional to the color-mixture curves for the three spectral colors, 425 mμ, 530 mμ, and 650 mμ, then the projection of the superimposed colored transparencies will result in perfect color reproduction. If transparent images of the colors described above, but having only half of the density specified for the transparencies, are printed in superposition on an opaque white support, and if the resulting color print is viewed with an illumination consisting of a white mixture of the three spectral colors, another perfect color reproduction will be secured.

The elementary principles of subtractive color reproduction are embodied in the preceding

paragraph. Unfortunately, the rigid requirements given there for the absorptions of the yellow, magenta, and cyan images, and for the illumination consisting of a white mixture of three pure spectral colors are quite impractical. As a result, such an elementary discussion of subtractive color reproduction is quite inapplicable to practical processes and requires modifications to adapt it to practically realizable materials and illuminants. These modifications make the details of the discussion much more complicated, but the main features are not difficult to understand. The first modification of the elementary discussion of subtractive reproduction is straightforward if the continued use of the white mixture of the three pure spectral colors as an illuminant is temporarily assumed. This modification is required because no dyes exist that absorb one wave-length without absorbing appreciable amounts of other quite different wave-lengths.

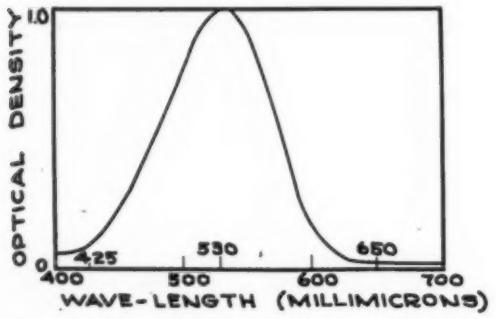

FIG. 9. Spectral density curve for a typical magenta dye.

The (optical) density of a deposit of any dye or mixture of dyes is defined for any wave-length as the common logarithm of the reciprocal of the transmittance of the deposit for that wave-length. For almost every pure, transparent, stable dye, the ratio of the densities for any two wave-lengths is a constant independent of moderate variations of the concentration of the dye. At every wave-length the density of superimposed or mixed deposits of several chemically nonreacting dyes is the sum of the densities of the same concentrations of the constituent dyes in separate deposits. Fig. 8 represents the density of a deposit of a typical yellow dye used for subtractive color reproduction. The concentration of this deposit is such that the density of the dye at 425 mμ is 1.0. In other words, only one-tenth of the incident blue light having wave-length 425 mμ is transmitted by this deposit. It will be seen that the density of this yellow deposit for the green unitary color (530 mμ) is 0.003 and that the density of this yellow deposit for the red unitary color (650 mμ) is 0.001. These undesired absorptions of the green and red unitary colors by the yellow dye are not of serious magnitude and could be ignored in practice. On the other hand, the undesired absorptions of available magenta (Fig. 9) and cyan (Fig. 10) dyes are much more serious and result in quite noticeable errors in uncorrected subtractive color reproduction. The ratios of the undesired to the desired densities for these dyes and unitary colors are shown in Table I.

TABLE I. *Densities of subtractive printing dyes for indicated wave-lengths.*

DYE COLOR	425 mμ	530 mμ	650 mμ
Yellow	1.000	0.003	0.001
Magenta	0.088	1.000	0.024
Cyan	0.225	0.288	1.000

If the density of the yellow dye deposited at any point in a subtractive color reproduction is measured by the density, D_y, of that dye alone for 425 mμ, and if the densities of the magenta and cyan dyes are measured, respectively, by the density, D_m, of the magenta for 530 mμ and the density, D_c, of the cyan for 650 mμ, then the density of the corresponding point in the subtractive reproduction will be the sum of the densities

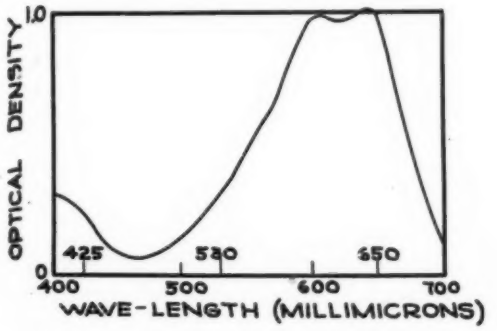

FIG. 10. Spectral density curve for a typical cyan dye.

of each of the constituent dyes for the corresponding unitary color. The density for the blue unitary color is

$$D_b = D_y + 0.088D_m + 0.225D_c. \quad (1)$$

The density for the green unitary color is

$$D_g = 0.003D_y + D_m + 0.288D_c. \quad (2)$$

The density for the red unitary color is

$$D_r = 0.001D_y + 0.024D_m + D_c. \quad (3)$$

The coefficients in these equations are taken directly from Table I.

A perfect duplication of the correct reproduction secured by the additive projection of the original gray transparencies will be secured if the densities D_b, D_g, and D_r are exactly the densities of the corresponding points in the gray transparencies. In order to determine what densities of the dyes should be deposited for perfect color reproduction, let us set D_b, D_g, and D_r equal to the densities of the corresponding gray transparencies suitable for a perfect additive color reproduction by the method of triple projection. Then, by solution of the three simultaneous linear equations, the proper densities of the dyes are

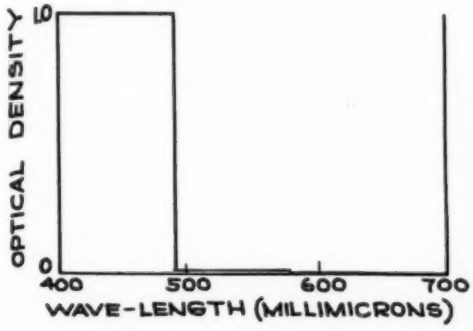

FIG. 11. Spectral density curve for a hypothetical yellow dye.

found to be

$$D_y = 1.000(D_b - 0.088D_g - 0.201D_r), \quad (4)$$

$$D_m = 1.007(-0.003D_b + D_g - 0.287D_r), \quad (5)$$

and $$D_c = 1.007(-0.001D_b - 0.024D_g + D_r). \quad (6)$$

A yellow image having the density specified by Eq. (4) can be printed from the negative having its sensitivity proportional to the color-mixture curve for the blue (425 mμ) unitary color if, in contact with this negative, there are placed

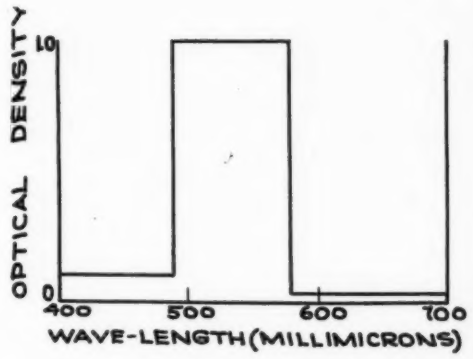

FIG. 12. Spectral density curve for a hypothetical magenta dye.

low contrast (flat) positive transparencies from the "green" and the "red" separation negatives. The correction transparency (called a mask) made from the negative having its spectral sensitivity proportional to the color-mixture curve for the green (530 mμ) unitary color should have a contrast of 0.088, equal to the coefficient of D_g in Eq. (4). Similarly, the mask made from the negative having its spectral sensitivity proportional to the color-mixture curve for the red (650 mμ) unitary color should have a contrast of 0.201. These masks serve to decrease the amount of yellow dye deposited in the printed image, corresponding to the blue absorptions of the magenta and cyan dyes which are to be superimposed on the yellow. Of course, masks whose computed contrasts are less than 0.1, for instance, the first mask mentioned above, can be omitted without appreciable error.

The magenta image having the density specified by Eq. (5) should be printed from the "green" separation negative, on which have been placed masks from the "blue" and the "red" separation negatives. These masks have contrasts of 0.003 and 0.287, respectively, as given by the coefficients of D_b and D_r in Eq. (5). As before, the first of these masks, having a contrast of less than 0.1, can be omitted. The cyan image having the density specified by Eq. (6) should be printed from the "red" separation negative, on

which have been placed masks from the "blue" and the "green" separation negatives, having contrasts of 0.001 and 0.024, respectively. In this case, both masks have contrasts of less than 0.1. Both masks can therefore be omitted, and the cyan image can be printed directly from the "red" separation negative.

The reproduction secured by the method just described will be quite satisfactory even if the

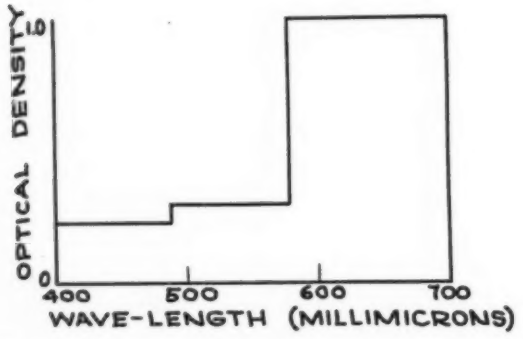

FIG. 13. Spectral density curve for a hypothetical cyan dye. The use of the masking method of correction with this cyan dye and with the hypothetical yellow and magenta dyes shown in Figs. 11 and 12 would result in perfect subtractive color reproduction.

reproduction is viewed in ordinary white light. It would be perfect in ordinary white light if the yellow, magenta, and cyan dyes had spectral absorptions of the kind shown in Figs. 11, 12, and 13. The spectral sensitivities for use with such dyes should be proportional to the color-mixture curves for the unitary colors consisting of the three wave-length bands from the illuminant, extending from 380 mμ to 490 mμ, from 490 mμ to 580 mμ, and from 580 mμ to 750 mμ.[6] Each of these unitary colors would remain unchanged in quality for all densities and mixtures of the dyes having the curves shown in Figs. 11, 12, and 13. The entire discussion for the pure spectral unitary colors would apply without alteration to subtractive reproductions employing such dyes, in any kind of white light. Such dyes are not obtainable, but the fact that the most suitable unitary colors and, consequently, the most suitable spectral sensitivities are determined by the absorption characteristics of the dyes in this hypothetical case indicates that practical dyes may also influence the choice of unitary colors.

A method for the identification of the unitary colors most suitable for use with any obtainable subtractive printing colors has been discovered.[14] In general, the unitary colors that are most suitable need not be physically realizable colors. These colors are used only as the bases for computing the spectral sensitivities and the masking contrasts most suitable for use with any particular set of printing colors. The computations involved are lengthy, but not difficult, and once carried out for any particular set of printing colors, they need never be repeated. Frequently, the unitary colors identified as most suitable are of greater saturation than the spectral colors of the same hue. Consequently, the magnitudes of the negative portions of the color-mixture curves frequently become negligible. The spectral sensitivities corresponding to such saturated unitary colors should only be used in conjunction with the corresponding masking corrections, for otherwise, the reproductions will be much too dark and unsaturated. The postulate of the additivity of densities on which the masking equations are based is not exactly realized with obtainable dyes in ordinary white light. However, when the unitary colors are suitably chosen, the principle of additivity gives good approximations to the color densities actually obtained with the best sets of dyes.

Like subtractive printing,[17] the masking method of correction was discovered[18, 19] and practiced empirically for many years before any investigation of the optical behavior of subtractive reproductions was carried out. The outline given in this paper indicates that physical reasoning is quite appropriate to such an investigation. All of the optical problems presented by color photography might have been the subjects of less trial and error and of more rapid and certain systematic solution if physical reasoning had not been rejected as inapplicable to color photography. Unsolved physical problems arise continually as new processes and new applications reveal new aspects of the fascinatingly intricate science of color reproduction. The renewal of active cooperation between photographers, chemists, and physicists may yet contribute greatly to the perfection of color reproduction.

Bibliography

1. J. C. Maxwell, "Experiments on Colour as Perceived by the Eye, with Remarks on Colour Blindness," Trans. Roy. Soc. Edinburgh **21**, 275 (1857); "On the Theory of Three Primary Colours," Proc. Roy. Inst. **3**, 370–374 (1858–62).
2. J. C. Maxwell, "The Theory of Compound Colours," Phil. Trans. **150**, 57–84 (1860).
3. *Handbook of Colorimetry* (Technology Press, Cambridge, Massachusetts, 1936), p. 7.
4. *Handbook of Colorimetry*, p. 49.
5. F. E. Ives, "Some Recent Advances in Photography," J. Frank. Inst. **125**, 345 (1888); "Heliochromy," J. Frank. Inst. **127**, 54 (1889).
6. A. C. Hardy and F. L. Wurzburg, Jr., "The Theory of Three-Color Reproduction," J. Opt. Soc. Am. **27**, 227 (1937).
7. D. L. MacAdam, "Photographic Aspects of the Theory of Three-Color Reproduction," J. Opt. Soc. Am. **28**, 412–416 (1938).
8. A. J. Bull and A. C. Jolley, "The Functions of Tricolor Filters," Brit. J. Phot. **51**, 48 (1904); A. J. Bull, "The Principles of Trichromatic Photography," Brit. J. Phot. **52**, 448 (1905); A. J. Newton and A. J. Bull, "The Practical Performance of Tricolour Filters," Phot. J. **44**, 270 (1904).
9. A. J. Bull, "On Three-Colour Additive Photography," Phot. J. **75**, 71 (1935).
10. A. J. Bull, "Note on Colour Mixture Curves and Colour Sensation Curves of the Spectrum," Phot. J. **75**, 258 (1935).
11. A. van Kreveld, "Ein gesetz für die Schwärzungskurven bei Mischfarben," Zeits. f. wiss. Phot. **32**, 222 (1934).
12. D. L. MacAdam, "Photographic Aspects of the Theory of Three-Color Reproduction," J. Opt. Soc. Am. **28**, 402 (1938).
13. J. H. Webb, "Summation of Different Color Radiations by a Photographic Emulsion," J. Opt. Soc. Am. **26**, 12 (1936).
14. D. A. Spencer, "Accuracy Attainable by Straight-Forward Colour Reproduction, Part 2, Filters for Subtractive Colour Photography," Phot. J. **75**, 377 (1935).
15. D. L. MacAdam, "Subtractive Color Mixture and Color Reproduction," J. Opt. Soc. Am. **28**, 446 (1938).
16. J. A. C. Yule, "Theory of Subtractive Color Photography," J. Opt. Soc. Am. **28**, 419, 481 (1938).
17. H. Collen, "Natural Colour in Photography," Brit. J. Phot. **12**, 547, 600 (1865); C. Cros, "General Solution of the Problem of Heliochromy," Brit. J. Phot. **16**, 426 (1869); L. D. du Hauron, French Patent 83,061 (1868) also pamphlet entitled "Les Couleurs in Photographie. Solution du Problème" (published by Marion, 1869).
18. E. Albert, German Patent 101,379 (1899); 116,538 (1900).
19. A. Murray, "Masking Method of Color Correction Applied to Three- and Four-Color Reproduction," Photoengravers Bulletin **23**, 13 (Jan. 1934); "The Modern Masking Method of Correct Color Reproduction," (Eastman Kodak Company, Rochester, New York, 1937).

The Design of Wide-Aperture Photographic Objectives

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THE modern "high speed" wide-aperture photographic objective is the latest stage in a long continued progression of small advances and improvements by a considerable number of workers in various parts of the world. The demand for greater speed has been with us as long as photography has been practised, and today the photographer is apparently still not satisfied with an aperture of even f : 1.5.

No photographic lens can be designed by the haphazard assembling of a number of positive and negative elements in a tube. There are too many conflicting conditions to be met for this method to be even a remote possibility, and it is only by studying the many principles and tendencies underlying lens action that one may hope to design a satisfactory system.

Most lenses have very obviously been developed from some prior design, incorporating the same principles that were used therein with additional features. Occasionally, however, a genius appears on the scene with an entirely novel type of construction which at once simplifies the problem and opens the door to many far-reaching improvements. Such were J. Petzval, with his portrait lens; J. H. Dallmeyer, with his rapid rectilinear; P. Rudolph, with his "principle of opposed gradation of refractive indices" and his double Gauss-lens Planar design; and lastly H. Dennis Taylor, with his airspaced triplet Cooke lens. Many others have contributed to the ever-growing volume of knowledge of the properties of lenses and the means by which their various aberrations may be removed.

Lens Speed

According to the elementary theory of image brightness, the illumination at the axial point of the image formed by a perfect lens free from aberrations or other defects is given by

$$E = k\pi B \sin^2 \theta, \qquad (1)$$

where B is the intrinsic brightness of the object (assumed plane) as measured from the lens position, k is the lens transmission, and θ is the slope of the extreme ray proceeding from the lens to the image-point in question. In applying this equation it is necessary to use homogeneous units, such as foot-candles for E and candles per square foot for B, or centimeter candles for E, and candles per square centimeter for B.

From the "sine condition" of Abbe, it is known that in a perfectly corrected lens the second "principal plane" will be in reality a portion of a sphere* centered about the focal point of the lens, of radius equal to the focal length. Each ray in a solid beam of parallel light entering a perfectly corrected lens from a distant axial object point will therefore be effectively bent by the lens at a point on the surface of this sphere, as shown in Fig. 1. Thus, the factor $\sin^2 \theta$ in the expression for the image illumination (Eq. (1)) becomes equal to $(y/f)^2$, and hence the image illumination is inversely proportional to the square of the ratio of the focal length of the lens to its effective front aperture. This ratio is called the f number of the lens, and the lens speed is thus inversely proportional to the (f number)^2. This statement is true out to the utmost limit of speed namely f : 0.5, in which case $\theta = 90°$ and the extreme emerging ray would be running just tangential to the image plane. This limiting

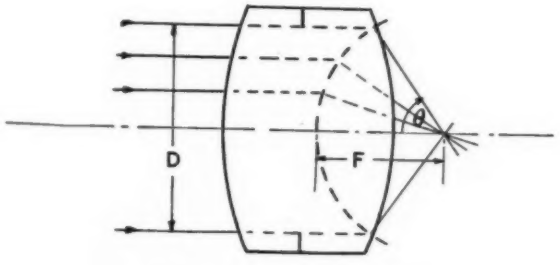

FIG. 1. The "speed" of a lens.

* It might be added that in a lens designed to be perfectly corrected at finite magnification, the two "principal planes" become parts of spheres centered about the two conjugate points.

speed is, of course, unattainable, but it has been approached in some special lenses used for astronomical photography which are really microscope objectives in which the light enters at the long conjugate end.

The data in Table I may be of interest in correlating lens speeds as expressed by the f number and by the microscopist's "numerical aperture." In the last line the relative speed of the lens is given, compared with f : 16 as unity.

The Difficulties of Securing High Speed in a Lens

No lens which operates well at, say f : 8, can be made merely of larger diameter to give it greater speed, even if the thicknesses were great enough to allow of the desired extra diameter. The chief factor which prevents this is the rapid rate at which spherical aberration increases with aperture. Suppose we take any reputable lens of aperture f : 8 and trace a number of parallel rays through it. If the entering rays are parallel to the axis, we shall find that the curve, connecting the height of incidence y with the distance s' from the back of the lens to the point at which the ray crosses the axis, has the shape indicated in Fig. 2. This phenomenon is known as spherical aberration. In this particular case, which represents the well-known "Dagor" lens of von Höegh, the aberration is zero for a ray entering at a height of 6.4 mm (f : 7.8) on 100 mm focal length, but for an intermediate aperture the lens has an "undercorrected zonal aberration" of almost 1 mm, and, for greater apertures, the lens is badly overcorrected. It is true that with some rearrangement of the surface powers within the lens a larger aperture might be achieved, but this would be only at the expense of much increased zonal aberration.

Thus, we may generalize by saying that any particular type of lens construction has what is virtually a limiting aperture beyond which it is not practical to go. This limit can be increased in some cases, by making considerable changes in the choice of glass, but no very great improvement may be expected in this way.

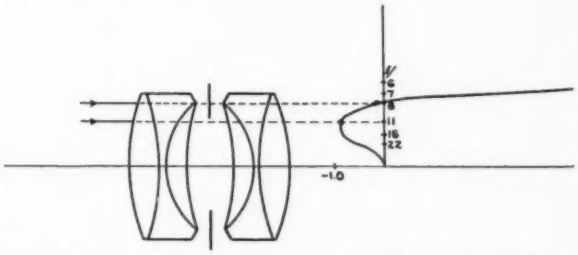

FIG. 2. Spherical aberration curve of original Dagor lens. (Ger. 74437, 1892.)

The ultimate cause of this zonal aberration is the disproportion in the rate of increase of spherical aberration with the "angular refraction," or the difference between the angles of incidence and refraction of the ray at the various lens surfaces. This rate is almost linear for small angles of incidence, but, for an angle of incidence of 45°, the aberration arising may perhaps be twice what it would be at an angle of only 35°. Consequently, if larger apertures are desired, the angular refraction of the extreme marginal ray must be kept as small as possible at every surface. It will be evident that in the three types analyzed in Table II, the first lens will be likely to have less zonal aberration than the other two. This is borne out by the aberration curves shown alongside the lens diagrams in Fig. 3.

Aberration Tolerances

The permissible tolerance of an aberration is determined by the amount that may be present before its effect becomes noticeable in a photograph taken with the lens. This is necessarily a

TABLE I. *Relative speeds of lenses.*

θ	1°.8	3°.6	5°.1	7°.2	10°.2	14°.5	19°.5	30°	56°.4	90°
f number $=\frac{1}{2 \sin \theta}$	16	8	5.6	4	2.8	2.0	1.5	1.0	0.6	0.5
Numerical aperture $=\sin \theta$	0.0312	0.0625	0.0884	0.1250	0.1768	0.25	0.3333	0.50	0.8333	1
Relative speed $=\left(\frac{16}{f \text{ number}}\right)^2$	1	4	8	16	32	64	114	256	711	1024

TABLE II. *Data on f : 3.5 ray through Petzval portrait lens.**

Surface	Angles of Incidence and Refraction (degrees)		Contribution to Spherical Aberration ($f=100$)
1	14.8	9.7	−1.26
2	24.1	23.1	+1.54
3	2.4	3.8	−0.07
4	0	0	0
5	10.0	15.9	+1.24
6	12.9	8.5	−0.60
7	7.9	12.0	−0.98
			Total −0.13
*Data on f : 3.5 ray through f : 3 Cooke-type lens.***			
1	21.0	12.8	− 3.54
2	9.7	15.8	− 3.15
3	28.9	17.2	12.44
4	14.3	23.8	4.33
5	10.0	6.2	− 0.34
6	16.8	28.0	−10.10
			Total − 0.36
Data on f : 3.5 ray through f : 2 planar-type lens.†			
1	12.6	7.8	−0.83
2	2.2	3.6	−0.07
3	11.2	6.9	−0.06
4	10.5	10.8	−0.13
5	11.2	17.8	+1.12
6	24.5	15.3	+5.13
7	5.1	5.0	−0.01
8	11.8	19.3	−2.75
9	2.5	1.5	+0.02
10	10.7	17.4	−2.80
			Total −0.38

* Zeits. f. Instrumentenk. **21**, 49 (1901).
** Brit. Pat. 155,640 (1919).
† Brit. Pat. 157,040 (1920).

somewhat indefinite quantity, especially as some aberrations, such as spherical, produce the effect of a loss of *contrast* rather than of a loss of *definition*. The tolerance for curvature of field, which is equivalent to a direct error in focus for the outer parts of the picture, is much more easily stated, because if our eyes are unable to distinguish between a perfect point image and a small circle of confusion of diameter c, then the curvature of field may be of such an amount as to throw the image out-of-focus by an amount equal to $\pm c \times (f \text{ number})$. Thus, if c is 1/500 inch (1/20 mm), and the f number is 4.5, we may have a curvature of field as great as 1/110 inch (1/5 mm). On the other hand, at $f : 2$, this limit becomes halved, so that, as the lens becomes more difficult to design, the tolerances at the same time become smaller, and our problem becomes doubly difficult to solve.

Microscope Objectives

Some of the earliest high speed achromatic lenses to be properly designed were the microscope objectives. The problem here is to secure the best possible spherical correction at the largest possible aperture, the only other requirement ordinarily considered (besides achromatism) being the fulfillment of the sine condition, which ensures that all zones of the lens shall yield the same image magnification. The earliest kinds of microscope objectives were merely small telescope objectives mounted together in close

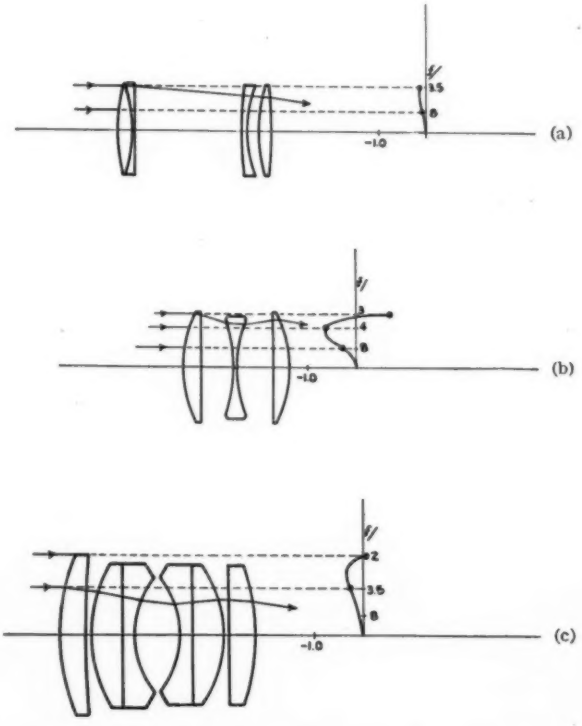

FIG. 3. Some spherical aberration curves: (a) $f : 3.5$ portrait lens (Zeits. f. Instrumentenk. **21**, 49 (1901)); (b) $f : 3$ triplet lens (Brit. 155,640 (1919)); (c) $f : 2$ planar-type lens (Brit. 157,040 (1920)).

succession, but Lister, the father of the famous Lord Lister, discovered that a better objective could be made by using two cemented doublets at a finite separation, which were such that each doublet was spherically corrected, and the coma contribution from one was equal and opposite to

that from the other.* In this way he obtained an $f:2$ lens (N.A.$=0.25$) which covered the necessary field of 1° or so very satisfactorily.

In later microscope objectives, a thick plano-convex lens was added in front of the two cemented doublets to increase the numerical aperture (Amici), and in the oil-immersion objective introduced by Abbe, a hyperhemisphere, followed by a simple meniscus lens, was used in front of the doublets. (Fig. 4). In these types it is possible to secure a numerical aperture as high as 0.95 for the dry lens and 1.4 for the oil immersion lens. These values correspond to $f:526$ and $f:0.357$, respectively. It will be noticed that when the short conjugate is filled with oil of index n, the maximum possible relative aperture has an f number of $1/2n$, and for $n=1.52$, this amounts to $f:0.328$. With dry lenses, as has been mentioned, the greatest possible speed is $f:0.5$.

In 1934, Rayton made an enlarged microscope objective of N.A.$=0.85$ ($f:0.59$) to an 8-times scale, having a focal length of 32 mm instead of the normal 4 mm. A concave lens had also to be added to convert parallel light into light diverging from the correct magnified tube-length distance on the long conjugate side. This has been used extensively at Mount Wilson to photograph faint stellar spectra. In 1936, Bracey designed a similarly enlarged oil-immersion objective of N.A.$=1.35$ ($f:0.37$) and 16 mm focal length, but in spite of its high speed, it is of limited use on account of its very short focal length. The photographic plate must, of course, be oiled to the back of this lens with cedar oil.

Means for Reducing Zonal Aberration

It has already been indicated that low zonal spherical aberration, and hence high apertures, can be obtained only if the angles of incidence of the marginal ray at all the surfaces can be kept small. This can be done by using only surfaces of long radius, and this is the secret of the Petzval portait-type of lens. On the other hand, to cover a wide field, we cannot always have long radii, and it then becomes necessary to consider the factors which determine how much spherical aberration will arise at each surface in a lens.

* There is thus no essential difference between the Lister microscope objective and the Petzval portrait lens, except that in the latter the separation and distribution of power between the two elements has been changed in order to widen the field at the expense of aperture.

It can be proved that the contribution of a surface to the spherical aberration depends on the difference between the angles of incidence and refraction, and also on the difference between the angle of refraction and the slope-angle of the ray as it enters the surface. Thus, any surface at which the marginal ray enters along the normal and is not refracted will contribute nothing to the spherical aberration† or to the coma, although that surface will add its due quota to the lens power, and will contribute strongly to the astigmatism in the lens. Similarly, if a surface is such that the angle of refraction is equal to the incident ray-slope, we have what is called an "aplanatic" surface,** which will contribute nothing to the spherical aberration, coma, or astigmatism. Considerable use is made of both "zero-refraction" and "aplanatic" surfaces, especially in high aperture microscope objectives and in some types of photographic lens. Unfortunately, a photographic lens cannot be constructed entirely of these aberrationless surfaces because the "zero-refracting" surface does not affect the convergence of the rays, and the "aplanatic" surface will only increase the convergence of converging light or increase the divergence of diverging light. Thus, an "aplanatic lens" comprising one of each type of aberrationless surface can be utilized only to increase the convergence of already converging light without at the same time increasing its spherical aberration and coma. In Fig. 5 such a lens is shown, in

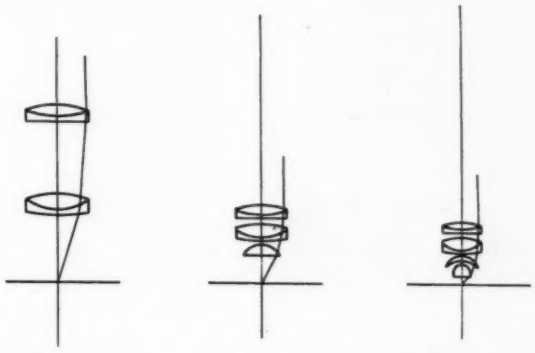

FIG. 4. Types of microscope objectives (schematic).

† As, for instance, surface (4) in Fig. 3A.

** This condition arises when the object-distance at a surface is equal to $r(n'+n)/n$. An example is surface (3) in Fig. 3C.

which A is an aplanatic point and Z is a zero-refraction point. Two aplanatic points cannot be used in succession because, in this case, the emerging ray will be parallel to the entering ray and the two surfaces of the lens will have the same radius. The use of a meniscus-shaped lens in a converging beam is seen in Figs. 18 and 21. Also, the three surfaces following the front plane of an oil-immersion microscope objective are all either aplanatic or zero-refraction surfaces.

Choice of Optical Glass Types

The necessity of making a lens achromatic is also a limitation which it is impossible to ignore. It is well known that a particular type of optical glass can be defined roughly by stating its index for one wave-length and its v number or reciprocal dispersive power. Thus, it is the refractive indices of the various glasses used in a lens which determine its aberrations, and the dispersive powers which determine its state of achromatism, both as to image position and also as to image size. It is often possible to design a lens entirely by refractive indices, and at the end to select suitable dispersions to effect the desired achromatism, but this procedure implies the availability of a wide range of dispersions to each index used. At the present time, this range though not perhaps as wide as is desirable, is surprisingly great. For instance, in Table III are given some of the various v values available for each of several refractive indices, taken from Schott's current optical glass catalog.

Since the strength of surfaces required in a lens is reduced by raising the index, and is also reduced by widening the separation between the v values of the glasses used, it is clear that the designer would be helped by having glasses covering a wider range of v values than is indicated in Table III. The tendency today in glass works is therefore to try to raise the index for a given v, or raise the v for each given index. It does not necessarily follow that raising the glass indices will improve a lens, and indeed, in many modern designs, extremely low refractive indices have been employed for special purposes.

There is still the possibility that some plastic material may eventually be developed having unusual optical properties. Synthetic and natural crystals have occasionally been used in lenses, but the mechanical difficulties involved have prevented their widespread use. For the same reason it has not yet been found practical to use aspheric surfaces in regular production lenses, although a number of patents have appeared in which an aspheric surface is employed.

Requirements to be Satisfied in Lenses Intended to Cover a Wide Field

No matter how good a lens is on the axis, it may be quite useless at a finite field. Indeed, the parabolic mirror of a large astronomical telescope, which forms a mathematically perfect image on the axis, will cover satisfactorily an angular field of only a few minutes of arc before the image is blurred by the presence of coma. When this aberration is present, the image magnification for each zone of the lens is different; hence, the middle portion of the lens may form a sharp image of a single extra-axial object-point, but the other intermediate and outer zones will form little blurred circles which fall radially inside or outside the image formed by the middle area of the lens, giving a "coma" image of the shape shown in Fig. 6. The size of this comatic image is found to vary rapidly with aperture, but more or less uniformly with the distance of the image out from the center of the picture. Hence, coma becomes very much harder to eliminate as the relative aperture of the lens is increased. Coma is analogous to a kind of lateral spherical aberration, and for a satisfactory lens, it must be

TABLE III. *Some typical optical glasses.*

	$n=1.52$			$n=1.58$	
	n	v		n	v
PKS-1	1.517	70	SK-12	1.583	59
PK-2	1.518	65	BaLF-4	1.580	54
BK-8	1.520	64	BaF-3	1.583	46
BaLK-2	1.518	61	LF-3	1.582	42
ZK-2	1.521	60	LF-5	1.581	41
K-3	1.518	59			
K-4	1.519	57			
KzF-5	1.521	53			
KF-5	1.523	51			
	$n=1.61$			$n=1.67$	
	n	v		n	v
SK-4	1.613	59	SSK-5	1.658	51
SK-6	1.614	56	BaF-10	1.670	47
SK-9	1.614	55	BaSF-6	1.668	42
SSK-3	1.615	51	BaSF-2	1.665	36
BaF-7	1.608	46	SF-5	1.673	32
KzFS-1	1.613	44			
BaSF-3	1.607	40			
F-4	1.617	37			

corrected just as fully as spherical aberration itself.

Astigmatism is another very serious defect of a lens which is used to cover a finite field. When this aberration is present, the images of a radial line and of a tangential line in the outer parts of the field are produced at different distances from the lens, so that if one is in focus, the other is out of focus. The amount of astigmatism can be varied by changing the shapes and distribution of the elements within a lens and the glasses of which they are made, but it is found that, when the astigmatism has been eliminated, the image of a flat object falls on a curved surface. The radius of curvature ρ of the middle of this surface is given by the expression $1/\rho = -\Sigma(n'-n)/(nn'r)$, where n' and n are the refractive indices on right and left of each lens surface, and r is the radius of curvature of that surface. This theorem is named after Petzval, and, since in all photographic lenses we are striving to secure a flat image of a flat object, it is very necessary to ensure that ρ has a large value. It is worth noting that in a single thin lens, $\rho = -nf$, so that the radius of this "Petzval surface" is about 1.5 times the focal length. In most anastigmats, this sum has been reduced to the point where ρ/f may be numerically as high as 4 or 5.

As we have seen, when astigmatism is corrected, the whole image lies on the Petzval surface. It is also found that with overcorrected

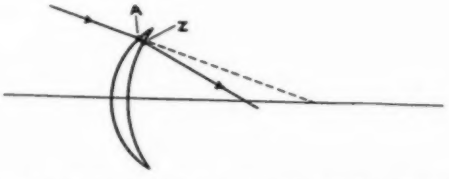

FIG. 5. An aplanatic lens in converging light. First surface aplanatic, second surface zero-refracting.

astigmatism, both tangential and radial focal lines lie beyond the Petzval surface, and with undercorrected astigmatism, both focal lines lie within it. This applies, strictly, to the middle parts of the field only, and in actual lenses the astigmatism varies considerably over the picture. Lenses are commonly designed to have perfect astigmatic correction on the axis and also at some particular obliquity, say 20°; the image is then allowed to take any form at obliquities between

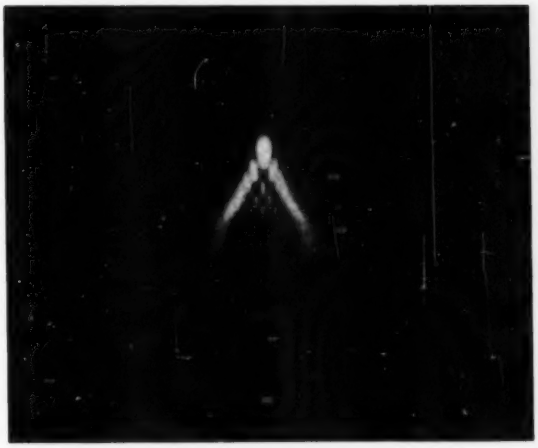

FIG. 6. A typical coma image.

0° and 20°. Sometimes these residual "field zones" of astigmatism are large enough to cause trouble, but generally this compromise is found to be satisfactory.

Anastigmat Lenses

Any lens system of which the construction is such that by proper design it is possible to increase the value of the ratio ρ/f, is now referred to as an "anastigmat." The degree of success achieved in designing the lens then produces a good or a bad anastigmat, but essentially the name "anastigmat" is given to any type of construction which is favorable to a reduction of the Petzval sum.

It is worth considering the three chief methods by which the Petzval sum $1/\rho = -\Sigma(n'-n)/(nn'r)$ can be reduced. It is clear that in a simple positive lens we ordinarily have an excess of positive power, lens power being $y(n'-n)/r$, where y is the ratio of the height at which a parallel entering paraxial ray strikes the surface r, to the height at which it enters the lens. Consequently, if we can make the parallel entering ray strike concave surfaces or negative lens elements lower than the height at which the same ray strikes convex surfaces or positive lenses, we shall be able to employ stronger concave surfaces or lenses and thus assist in reducing the Petzval sum.

As example of this, consider Fig. 7, which shows the outlines of four typical anastigmat types, and it will be seen how in each case the ray drops to a concave surface or lens and rises to a convex. Fortunately, this rising and falling

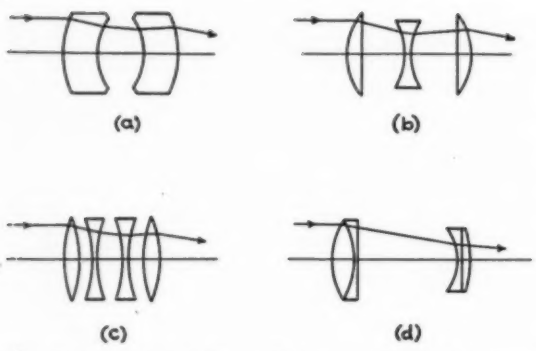

FIG. 7. Illustrating how the ray strikes the concave surfaces or elements lower than the convex surfaces or elements.

of a ray is a natural consequence of separating the surfaces or lenses by finite distances, and it is perfectly possible to overdo the correction and give a backward curving Petzval surface if the thicknesses or separations are made too great.

The three types shown in Fig. 7 (a), (b), and (c) are typical of practically all the anastigmat lenses, which can thus be classified naturally into two-, three-, and four-component types. In some examples, the designer has split a component to obtain better corrections without, however, altering the essential type of construction. The Petzval sum is thus seen to be the underlying and determining factor which has caused almost all photographic lenses to crystallize into one or other of these three fundamental types.

Distortion

One further aberration should be mentioned, namely distortion. This aberration refers to a variation in magnification over the field of the lens, and it may be corrected by redistributing the powers and separations of the various elements on the two sides of the stop, roughly as if balancing a lever by redistributing the sizes and the positions of weights on either side.

Oblique Spherical Aberration

It often happens that when all of the aberrations mentioned have been well corrected, the spherical aberration of the oblique beam is badly overcorrected although it was well corrected in the axial beam. This aberration is a particularly awkward one to correct, and necessitates considerable care in the choice of lens type for its elimination. For example, to eliminate it in the Planar type, Warmisham (U.S. 2,130,760 (1938)) suggested the addition of cemented collective surfaces close up to the concave surfaces on each side of the stop.

Unfortunately, the spherical aberration of an oblique pencil is mixed up with astigmatism so that the spherical aberration of rays in the primary plane (i.e., the plane of the usual lens diagram containing the object point) is different from the spherical aberration of the secondary rays (which are skew rays lying entirely outside of the plane of the diagram) and because the vignetting or cutting down of an oblique beam by the front and rear lens apertures reduces the size of the beam in the primary plane much more drastically than in the secondary direction, the skew rays may become more important than the ordinary primary rays. The problem is rendered much more troublesome by the mathematical difficulties in the computation of skew rays as compared with rays in the primary plane, and because there are so many of them.

Approximate Sizes of Lens Fields

A lens designed to work solely on the axis, such as a telescope objective, may be said to cover zero field. A low power microscope objective sometimes covers a field of 2° or 3°; projection and portrait lenses usually cover from 5° to 10° off the axis, depending on the design and the particular application; motion picture lenses cover a semi-field of 14° to 16°, and regular camera lenses cover 20° to 26°. Wide angle lenses go from 25° up to 35°, and extra wide angle lenses go sometimes as far as 45° from the lens axis. As the requirements to be satisfied in wide aperture lenses and wide field lenses are usually incompatible, we find that wide angle lenses cannot usually be operated at a greater speed than about $f:4$, and extra wide angle lenses cannot be made beyond $f:6.3$. There are a few exceptional wide angle lenses that work at $f:3.5$ or $f:2.7$. In Fig. 8 are shown the angles covered by different types of lens, against each being indicated the maximum aperture that can normally be obtained for that field.

Symmetrical Lenses

It can readily be shown that a lens which has complete symmetry about the center of the stop,

and operating at unit magnification, will be automatically free from the transverse aberrations, distortion, coma, and chromatic difference of magnification. The designer has then to consider only the longitudinal aberrations, spherical, chromatic, field curvature, and astigmatism.

If such a perfectly symmetrical system is now used at unequal conjugates, for example, with an infinitely distant object, all the corrections will be upset, although the transverse aberrations will ordinarily not become great. A large number of symmetrical lenses have been designed in which this principle is employed, but it is found that some departure from strict symmetry is always advisable to allow of better corrections with infinite objects. At the present time, the only lenses in which complete or approximate symmetry is used are the wide angle lenses of aperture not greater than about $f:5$. Nevertheless, a number of successful high speed lenses have been derived from symmetrical types by the introduction of a considerable degree of asymmetry.

Some Wide Aperture Lens Types

While there are two or three textbooks which give a fairly complete survey of the trend of design in photographic objectives, it is probably true that the patent files provide the best source

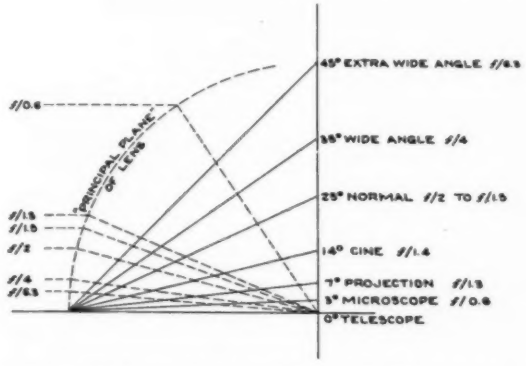

FIG. 8. Typical apertures and fields of different types of lens.

of information as to the construction of the various lens types and the reasons why each particular form was tried. For this reason, in the following survey repeated references will be made to published patent specifications as a means of definitely identifying the various lenses mentioned.

Practically all high speed photographic lenses are developed from one of three types, namely the Petzval portrait lens, the triplet air-spaced type (the Cooke lens), and the four-piece air-spaced type. Some few examples are borderline cases and cannot be definitely classified in any one of these groups, and in some designs a front member of one type has been combined with a rear member of another type. The trend of development in each group will be outlined separately.

Types Derived from the Petzval Portrait Lens

The construction of the original portrait lens designed by Petzval in 1841 is shown in Fig. 3(a). This lens could be operated at $f:3.5$ and cover about 12° satisfactorily. On account of its excellent central definition, it has remained the most popular form of lens for all cases where a small angular field is sufficient, such as in motion picture projection and in long focus motion picture taking lenses. In this type, reduction of the Petzval sum is impossible because the positive and negative elements in each component are mounted closely together. Each component is separately achromatic, and also approximately spherically corrected to reduce the zonal residuals. The remaining degrees of freedom in the design are (a) the distribution of power between the two components, (b) the width of the central space, and (c) the difference in curvature on the two sides of the rear narrow airgap, which are used to correct coma and distortion, and to obtain the most favorable amount of overcorrected astigmatism to compensate the uncorrected Petzval sum. This type was improved from time to time during the last century, notably, by Zincke Sommer in 1870, who raised the aperture to $f:2.3$, and by Voigtländer, in 1878, who was able to cement the two rear elements together by sacrificing some of the spherical correction in the front component. Some recent further improvements are shown in Fig. 9. In Fig. 9(d) is shown the addition of a negative Piazzi-Smythe "field flattener" to a lens of this type by which the Petzval sum can be much improved and the field appreciably flattened.

A very real improvement can be made by introducing air-spaces between the elements of

both components, and by using barium crown instead of common crown glass. This not only improves the Petzval sum but provides a number of additional degrees of freedom which may be utilized to reduce zones. A typical example is the $f:2$ of Frederick and Altman shown in Fig. 10, which covers to about 12°, with almost

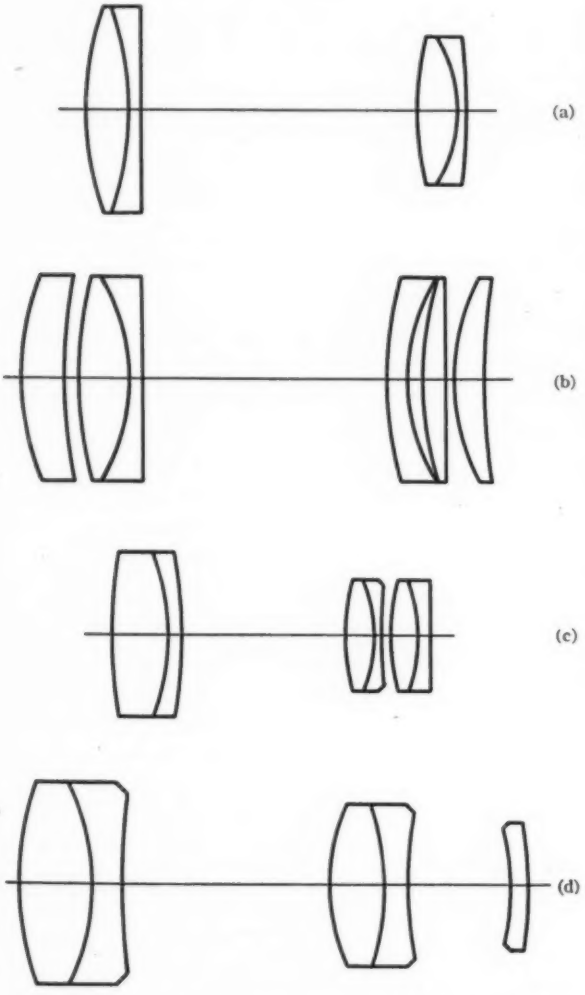

FIG. 9. Modifications of the portrait lens type: (a) Zeiss $f:1.9$ (Brit. 361,793 (1931)); (b) Warmisham $f:1.5$ (U.S. 1,797,202 (1931)); (c) Schade $f:1.3$ (U.S. 2,158,202 (1939)); (d) Wood $f:1.6$ (U.S. 2,076,190 (1937)).

no vignetting of oblique pencils. Urban in 1923 (U.S. 1,474,743) described a similar lens covering 14° at $f:2$, in which the air-spaces between elements had been made still wider. An extreme example of this plan is the R-Biotar of Merté (U.S. 1,967,836 (1934)) covering a few degrees of field at $f:0.85$, Fig. 11.

Types Developed from the Cooke Three-Component Lens

The original triplet was designed by H. Dennis Taylor in 1894 (U.S. 540,122 (1895)) and is shown in Fig. 12. Each element in this was separately achromatized and approximately spherically corrected. Later, Taylor realized that he could obtain adequate correction by the use of three single lenses (U.S. 568,052 (1896)). This extremely simple form was called the Cooke lens after the company with which Taylor was connected, and appeared in a series of forms from an $f:8$ covering a moderately wide angle, down to an $f:3.5$ for portraiture. The lens illustrated in Fig. 3(b) is a more recent example of this same type, and covers a 25° field at $f:3$.

The Cooke lens possesses just sufficient degrees of freedom to enable the designer to secure both kinds of achromatism and also a good compromise on the five principal types of aberration (spherical, coma, Petzval sum, astigmatism, and distortion). There are thus no spare variables that may be used to help reduce zonal residuals of any kind. To extend the aperture beyond $f:3$, it is therefore necessary to introduce some further lenses, as was done by Bielicke (U.S. 1,540,752 (1925)) and Lee (U.S.1,739,512 (1925)), who attained an aperture of $f:2.5$ by splitting the rear lens into two (Fig. 13). Most of the spherical undercorrection in the triplet type arises at the rear surface (see Table II second example), which must be compensated for by a large amount of overcorrection from surface 3. If

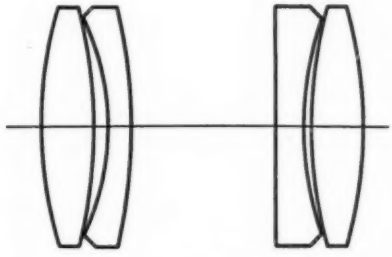

FIG. 10. Frederick and Altman $f:2$ (U.S. 1,620,337, 1927).

the rear surface is replaced by a much weaker surface plus another lens shaped so as to introduce but little aberration, then much less overcorrection will be necessary at surface 3, with consequent reduction of the zonal aberration

which is caused by the opposition of large positive and large negative aberrations arising at widely separated points in the system.

Many other attempts have been made to introduce more degrees of freedom into the triplet. The first and in some ways most successful was the Tessar lens of Rudolph (U.S. 721,240 (1903)), in which the rear element was composed of a cemented doublet having its collective cemented face convex to the stop, for the purpose of improving the oblique spherical aberration. The original design covered a semi-field of 30° at f : 5.5, and later designs by Rudolph and by many others have pressed the aperture up to f : 2.5. From some points of view the Tessar may be regarded as being developed from the 4-piece air-spaced type by cementing the rear lenses together. However, Rudolph states that he was led to this construction directly from his famous Protar lens of 1891 (U.S. 444,714), which consisted merely of two cemented doublets in one of which the contact face was concave to the stop and in the other convex to the stop. Rudolph's first step from this was to introduce a dispersive air-space into one-half and a collective air-space into the other half, giving the Unar of 1900 (U.S. 660,202), and from this latter lens the Tessar was developed by retaining the dispersive air-space in front, and going back to a collective cemented face in the rear element. (Fig. 14).

Every conceivable variant of the triplet appears to have been tried, a notable example being the Pentac f : 2.9 by Booth (Brit. 151,506), shown in Fig. 15, in which both convex elements of the triplet have been made into cemented doublets, with the cemented surface convex to the stop. Another well-known improvement is the Biotessar f : 2.7 of Wandersleb and Merté (U.S. 1,697,670 (1929)), shown in Fig. 16. Berek also has described a triplet in which all three lenses are doublets, for which an aperture of f : 2 is claimed (U.S. 1,939,098), shown in Fig. 17.

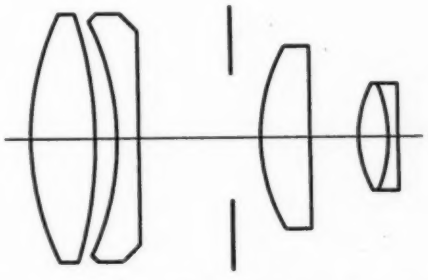

FIG. 11. Merté f : 0.85 (U.S. 1,967,836 (1934)).

Another interesting series of developments from the Cooke type are those by L. Bertele,

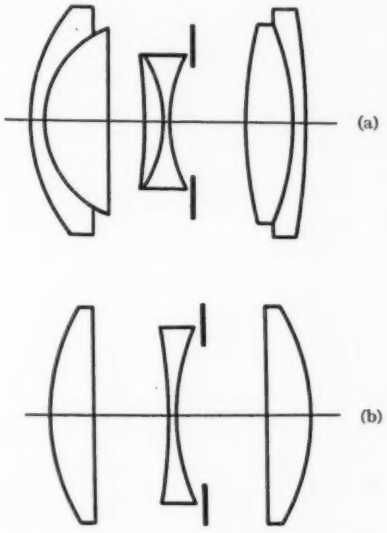

FIG. 12. The Taylor triplet lens: (a) Original form (U.S. 540,122 (1895); (b) the Cooke lens (U.S. 568,052 (1896)).

formerly of the Ernamann Company and now connected with Carl Zeiss. His plan was to weaken the rear face by taking power from the rear to the front, where it was added in the form of an approximately aplanatic meniscus-shaped lens immediately following the normal front lens (Fig. 18). The resulting distortion was then balanced out by increasing the rear air-space. This first design covered only a semi-field of 12°, but it was raised to 20° at f : 2.9 by making the added lens into a cemented doublet (Fig. 19). He then joined components (2) and (3) together, making them into a cemented triplet, obtaining a number of very practical and workable designs (Fig. 20). The lens illustrated in Fig. 20(c) is the well-known Sonnar f : 1.5 lens covering a semi-field of 24°. An interesting extension from Fig. 20(c) is found in the wide-angle Biogon f : 2.7 shown in Fig. 20(e).

By an extension of the same idea, Lee (U.S. 2,012,822 (1935)) has secured an aperture of f : 1.0 (Fig. 21) by using two positive meniscus lenses in close succession before the thick meniscus-shaped negative component.

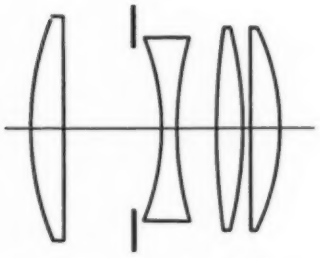

FIG. 13. Bielicke (U.S. 1,540,752 (1925)) and Lee (U.S. 1,739,512 (1925)), f : 2.5 lens.

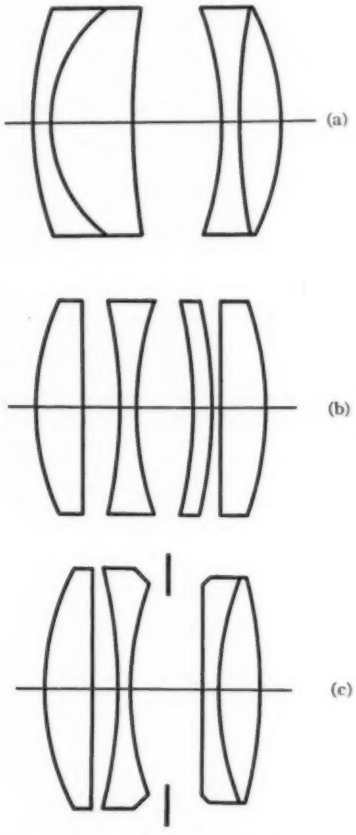

FIG. 14. The evolution of the Tessar lens: (a) Protar (U.S. 444,714 (1891)); (b) Unar (U.S. 660,202 (1900)); (c). Tessar (U.S. 721,240 (1903)).

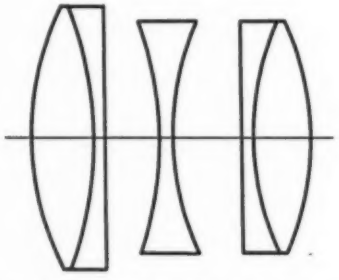

FIG. 15. Booth Pentac f : 2.9 (Brit. 151,506 (1919)).

Lenses of the Four-Component Air-Spaced Type

There are two independent series of four-component air-spaced lenses, one in which all the elements are biconvex or biconcave, and the other in which only meniscus lenses are used. These will be considered separately.

The first type appears to have originated in the Celor of Goerz and von Höegh, shown in Fig. 22, which covered an angle of 30° at f : 5. The type proved to be promising, and the aperture was raised to f : 3.5 by Zschokke (U.S. 912, 352 (1909)) by introducing a decided lack of symmetry between the two halves. Extreme

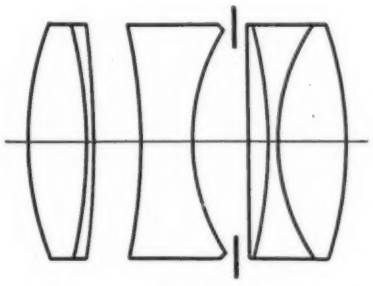

FIG. 16. Wandersleb and Merté f : 2.7 (U.S. 1,697,670 (1929)).

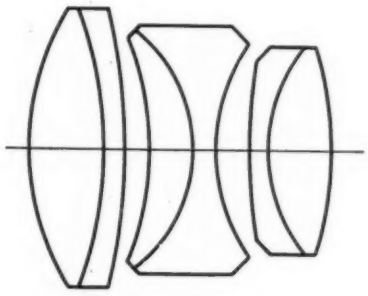

FIG. 17. Berek f : 2 (U.S. 1,939,098 (1932)).

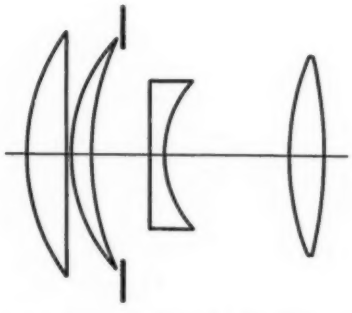

FIG. 18. Bertele f : 2 (Brit. 186,917 (1923)).

examples derived from this type are the Ernostar f : 1.8 of Bertele (Fig. 23) and the f : 1.0 lens of Warmisham (Fig. 24).

The second series of four-piece air-spaced lenses had its origin in the separated meniscus telescope objective of Gauss. Alvan Clark (U.S. 399,499 (1889)) had early suggested the combination of two Gauss objectives to make a photographic portrait lens, the field being flattened by experimental adjustment of the air-spaces (Fig. 25). The property of the Gauss objective which gives it its chief interest is that, with this type, it is possible by careful design to secure similar spherical correction in two different colors, thus securing virtually identical spherical aberration curves in all colors. This is far from the case in telescope objectives of the ordinary cemented type. Consequently, photographic objectives embodying lenses of the Gauss meniscus type can be designed so as to give a far higher order of "sphero-achromatism" than any other type. This type has therefore long been popular in process lenses for the photomechanical reproduction of colored pictures.

The first advance in the use of Gauss objectives was made in 1897 by Rudolph who attempted in his Planar lens (U.S. 583,336) to make a properly designed objective embodying this form of construction. He soon found that a satisfactory design at an aperture of f : 4 would require a

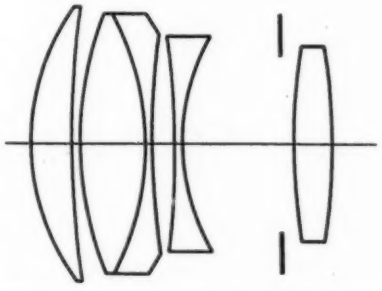

FIG. 19. Bertele f : 2.9 (Brit. 237,861 (1925)).

flint glass of higher dispersion than those readily available, so he divided the inner negative lenses into two of identical index but different dispersions, making them "hyperchromatic" (Fig. 26). Later, by modifying the design, simple negative lenses were substituted in the Meyer Aristostigmat f : 6.8 (Brit. 20,349, (1900)) and in the

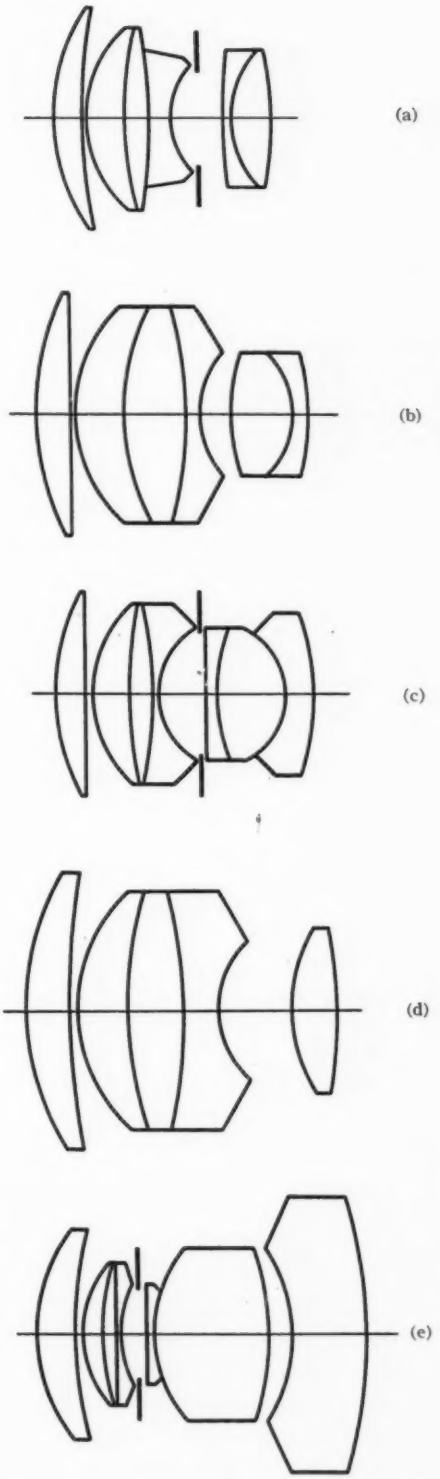

FIG. 20. Some recent Bertele designs: (a) f : 2 (Brit. 383,591 (1932)); (b) f : 1.4 (U.S. 2,029,806 (1935)); (c) f : 1.5 (U.S. 1,975,678 (1934)); (d) f : 1.2 (U.S. 2,141,733 (1937)); (e) f : 2.7 wide angle (U.S. 2,084,309 (1937)).

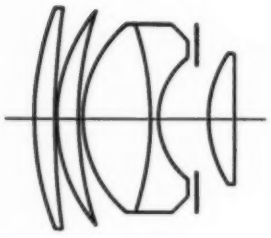

FIG. 21. Lee, f : 1.0 (U.S. 2,012,822 (1935)).

f : 4.5 Omnar by Martin (Austrian 8364, (1901)), shown in Fig. 27.

In Rudolph's planar lens, several important degrees of freedom had been lost by insisting that the two parts of the negative cemented doublet be of the same index, and also by requiring exact symmetry about the stop. In 1920, Lee succeeded in designing his remarkable "Opic" lens of aperture f : 2, covering the regular 24° semi-field (Fig. 28), by departing from strict symmetry and by introducing an index difference across the two cemented surfaces. This lens started a long line of designs of the same general type, in which apertures have reached f : 1.4 for motion picture purposes (Fig. 29), for a 12°

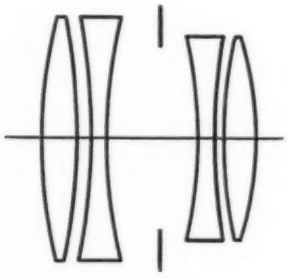

FIG. 22. Von Höegh Celor f : 5 (U.S. 635,472 (1899)).

field, but have not been made to exceed f : 2 for 25° fields except by splitting the rear lens into two close positive lenses (Fig. 30), or by the use of aspheric surfaces (Fig. 31). The real trouble with this type of construction appears to be bad spherical aberration of the oblique rays, particularly in the secondary plane, and until some means is found for overcoming this particularly troublesome defect, it is unlikely that greater apertures than these will be realized with this form of construction.

A few types have been described in which the negative elements are convex to the stop, of these the Kino-Plasmat f : 2 (Fig. 32), by Rudolph is noteworthy for a field not exceeding about 15°,

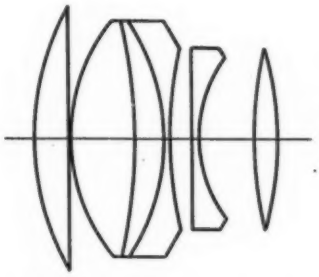

FIG. 23. Bertele Ernostar f : 1.9 (U.S. 1,708,863 (1929)).

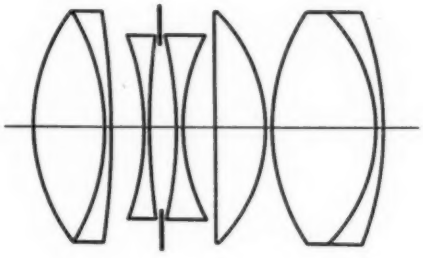

FIG. 24. Warmisham f : 1.0 (U.S. 1,926,569 (1933)).

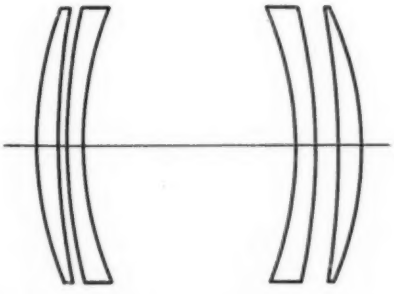

FIG. 25. Alvan Clark (U.S. 399,499 (1889)).

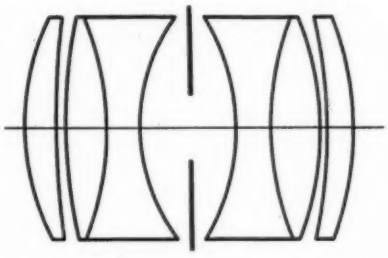

FIG. 26. Rudolph Planar f : 4 (U.S. 583,336 (1897)).

and also the similar design suggested in U.S. 1,833,593 (1931), (Fig. 33), in which an aperture of $f:1$ is achieved.

It will be noticed that a great many designs have been worked at and patented for lenses having an aperture between $f:1$ and $f:2$, yet there are only perhaps half a dozen lenses offered for sale which have an aperture in this range and cover a 25° semi-field, although for motion picture lenses there are considerably more types available in this aperture range. The conclusion is that these designs for some reason or other are unsatisfactory, or have not so far been worked out to a useful final form. This offers the designer both despair and hope; despair that he will ever succeed where so many have apparently failed, and hope because there are so many avenues of attack that have scarcely yet been touched. Even without revolutionary changes, such as the use of aspheric surfaces or the introduction of entirely new kinds of glass, we may hope to see many better and faster lenses available within the coming years.

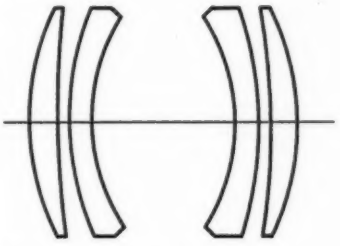

Fig. 27. Omnar and Aristostigmat, 1900.

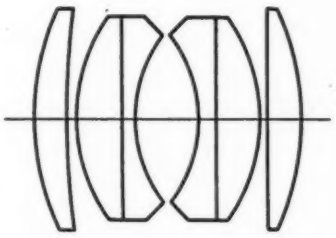

FIG. 28. Lee Opic $f:2$ (Brit. 157,040 (1921)).

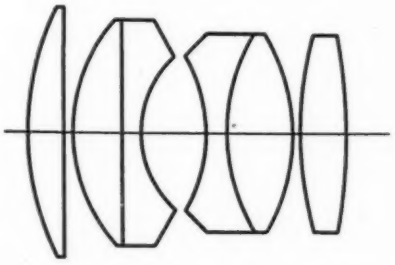

FIG. 29. Merté Biotar $f:1.4$ (U.S. 1,786,916 (1930)).

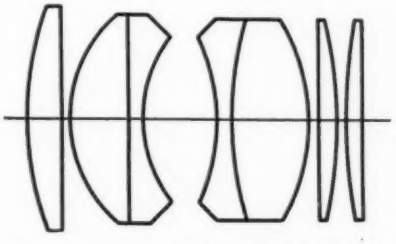

FIG. 30. Lee $f:1.4$ (U.S. 2,019,985 (1935)).

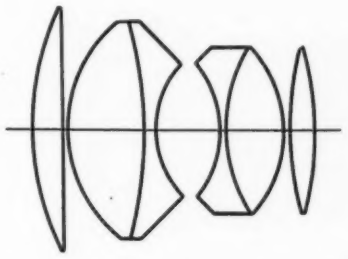

FIG. 31. Lee $f:1.1$, with aspheric rear surface (U.S. 2,100,290 (1937)).

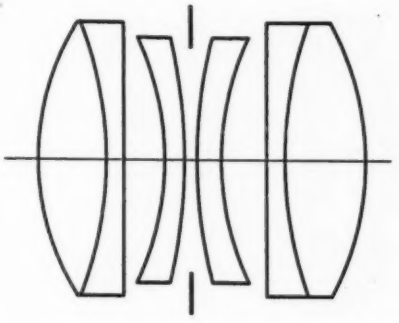

FIG. 32. Rudolph Kino Plasmat $f:2$ (U.S. 1,565,205 (1925)).

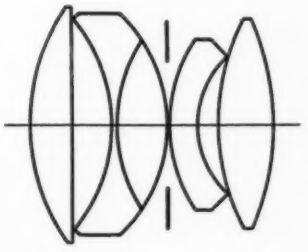

FIG. 33. Rudolph $f:1$ (U.S. 1,833,593 (1931)).

Resumés of Recent Research

Mechanism of Nuclear Fission

Following the discovery in 1935 by Fermi and his collaborators that neutrons can be captured by the nuclei of heavy atoms to form new radioactive isotopes, a great increase has taken place in the number of artificially produced radioactive substances and particularly in our understanding of the nature of nuclear reactions. Through the successes of Bohr's liquid-drop model of atomic nuclei it has come to be realized that nuclear transformations do not take place by the incident particle directly exciting another particle or by its directly radiating so much energy that it cannot escape, but rather in a two-step process. The first step consists in the formation of a compound nucleus which has a lifetime many times longer than the time which would be required for a free particle to cross the nucleus; for owing to the very strong interaction between the nuclear constituents the energy of the primary particle is quickly shared with all the neutrons and protons of the nucleus in a manner analogous to the distribution of thermal energy in a heated body, and no one particle will ordinarily possess enough energy to escape from the attraction of its neighbors. The second step in the reaction takes place when either one particle at the nuclear surface by a favorable fluctuation in the distribution of energy gains enough energy to "evaporate" or the nucleus as a whole radiates away a quantum of energy, ordinarily of such a magnitude that the compound system is then unable to evaporate any of its constituents and the incident particle is thus permanently captured.

When compared with this simple picture, the reactions produced by neutron bombardment of uranium and thorium, however, seemed for a time very complicated and obscure, until Hahn and Strassmann discovered that from uranium thus bombarded there are formed elements of much smaller atomic weight to which almost all of the complex of radioactive activities was due. This new type of nuclear reaction, later found also in thorium and protactinium, was given the name "fission" by Meitner and Frisch, who on the basis of the liquid-drop model of nuclei emphasized the analogy of the process concerned with the division of a fluid sphere into two smaller droplets as the result of an external disturbance.

A recent paper of Bohr and Wheeler[1] shows how fission takes its place among other nuclear reactions for which a satisfactory account can be given in terms of the liquid-drop model. The two-stage picture of the reaction is valid as previously; but for the second stage of the reaction, where before the compound nucleus was thought capable only of radiating away its energy or by chance concentrating enough of it on one particle at the surface to lead to evaporation, a new possibility is present for sufficiently heavy,

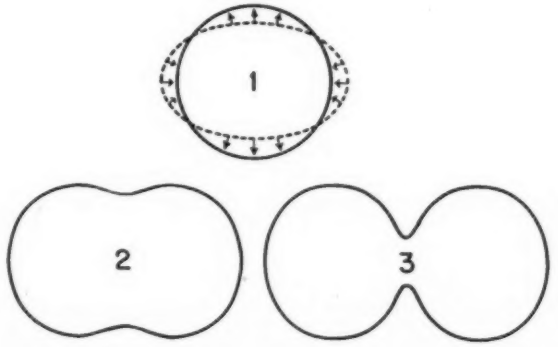

FIG. 1. Critical deformations leading to nuclear fission according to the liquid-drop model. A small distortion of the spherical form (1) leads to stable oscillations about the globular form, unless the droplet is so highly charged electrically (charge = (10 × surface tension × volume)$^{\frac{1}{2}}$) that even the slightest deformation makes it possible for the electrostatic repulsions to rupture the droplet. If the charge has less than this limiting value (as corresponds to the case of all actual nuclei) a finite deformation will be required to lead to a critical configuration of unstable equilibrium. This deformation is small (2) and the energy which a bombarding neutron must have to bring it about is not great for the most highly charged nuclei, but as the charge is diminished the deformation necessary to lead to rupture is greater (3) and fission is no longer possible for the bombarding energies obtainable.

[1] N. Bohr and J. A. Wheeler, Phys. Rev. **56**, 426 (1939).

highly charged nuclei. A chance fluctuation in the distribution of energy among the various degrees of freedom of the nucleus can lead to a deformation of the nucleus of sufficient magnitude (approximately an egg-shaped surface) that the mutual repulsion of the electric charges will overbalance the effect of the short range nuclear forces, analogous to that of surface tension in a liquid, and the nucleus will divide into two fragments whose electric repulsions will then drive them apart with high velocity. The potential energy necessary to produce such a critical deformation is closely analogous to the so-called "activation energy" of a monomolecular reaction; and in fact Bohr and Wheeler have calculated the absolute rate of the fission reaction by using many of the concepts familiar to physical chemists. The probability of fission turns out to depend not only on the incident neutron bringing enough energy to the compound nucleus to make possible a critical deformation but also on the latent heat of evaporation of a neutron being greater than or almost as great as this critical energy; otherwise a neutron will be sent out before there is time for fission and the nucleus will again lack the energy which is needed to lead to a critical deformation.

The same paper also investigates from the point of view of the liquid-drop model the problem of estimating how the energy required for a critical deformation will differ from one nucleus to another. The results indicate that uranium, thorium, and protactinium are the only available elements for which neutrons can be expected to produce fission. Occasionally, it is true, a uranium nucleus captures a neutron instead of dividing, and the new isotope, being radioactive, leads to element 93. What is the fate of these nuclei is still an unsolved question, but at any rate the liquid-drop theory of fission indicates that if stable they should be very susceptible to fission produced by neutrons.

New Books

Texts on Photography

Photography, Its Principles and Practice. C. B. NEBLETTE. Third Edition. Pp. 590+xi, Figs. 229, $15\frac{1}{2}\times23\frac{1}{2}$ cm. D. Van Nostrand Company, New York City, 1938. Price $6.50.

The Photographic Process. JULIAN ELLIS MACK AND MILES J. MARTIN. Pp. 586+xvii, Figs. 275, 18×25 cm. McGraw-Hill Company, New York City, 1939. Price $5.00.

Although photography has been recognized as a useful tool in the sciences for many years, and is an art in its own right, it has been only recently that the need for some sort of instruction in the art and science of photography has been generally recognized. Those who first started giving instruction in this field were confronted with the difficulty of teaching without an adequate text. The two books under consideration are designed to meet the need for a text, and in addition they approach the subject from two different standpoints, which should make it easier to find a reference book suited to one's own taste.

The first of these books, Neblette's *Photography*, approaches the subject from a somewhat advanced point of view. The author states in his preface, "The book presumes some knowledge of physics and chemistry. No attempt has been made, therefore, to explain in detail elementary concepts of either subject which may be necessary to the understanding of the text." It might be added that a knowledge of the rudiments of photographic technique would give one a greater appreciation of the book.

The author first gives a brief history of the development of photography. This section constitutes a fine survey of the field. In the next part, comprising roughly one-half of the book, the author deals mostly with the theory of the various photographic processes. He discusses here the camera, photographic optics and objectives, the photographic emulsion and its properties, reproduction of color in monochrome, and the theory of development. References are made to apparatus to tie the theory to practice. Of interest to some will be the discussion of the experimental technique involved in determining the characteristic curve for a photographic emulsion. The discussion of photographic objectives is, in general, good, though when the author discusses the simultaneous correction of astigmatism and spherical aberration he falls short of his goal because the symbols used in the text of the discussion do not match those in the accompanying figure.

The last half of the book is taken up with the details of photographic practice, such as processing of negatives, printing, toning, three-color photography, etc. Extensive discussion of typical formulae, methods of processing, and causes of common failures make this an excellent reference section even for the more experienced person.

This book makes a good reference as well as a text, though it should be remembered that it is not for those who are without any scientific background. The explanations are, in general, well written. The author has the convenient habit of enumerating or tabulating important points, which helps in clarifying the subject under discussion. This is a handy book to have.

The second book, Mack and Martin's *Photographic Process*, appears to have been written for a different type of student, namely, a student who has had little in the way of physics or chemistry and who wants to know what photography is all about. Hence the authors start explanations from elementary considerations and work up to the desired result. They also add, in small print, sections designed for perusal by the more advanced or ambitious reader who wants a more thorough treatment of the subject. This book cannot be nicely divided into sections dealing with theory and sections dealing with practice, as was the case with the first book, because the tendency in this book is to feed in the practice along with the theory. This habit puts the book of Mack and Martin more or less in the textbook class, as against Neblette's book, which is somewhat of a reference. Subjects covered are, of course, photographic optics, the camera, the photographic emulsion, exposure and development of the negative, printing, and color and color photography. In addition there are discussions of photomechanical reproduction, pictorial photography, and the uses of photography in various scientific fields. The last subject should appeal to many of the students. Not present in the book are discussions of commercial and studio practices, such as retouching, etc.

The paper used in the book is a high quality paper which takes photographs nicely, and gives an attractive appearance to the volume. This is of prime importance in a book on photography. A picture printed on poor paper loses its appeal and merely becomes a horrible example. Because of the choice of paper the book is very weighty indeed, literally speaking.

Outstanding is the set of laboratory experiments which are intended to be performed as the course proceeds. The experiments are well correlated with the text material, start with simple manipulations, and give the student a good understanding of photographic technique. This manual of experiments is a good answer to the students' cry for "practice." Also good are the appendices giving some background in chemistry and mathematics for those who need it, and a list of typical photographic formulae. Altogether, this is a good text for a general course in photography.

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Recent Booklets

The DuMont Oscillographer, publication of the Allen B. DuMont Laboratories, Inc., 2 Main Avenue, Passaic, New Jersey, devotes its August-September, 1939, issue to discussion of "The Amplification of Direct-Current Signals Through Alternating-Current Circuits" and "A New Stimulator for Brain-Surgery and Research."

The Educational Focus, Fall, 1939, edition, published by Bausch and Lomb Optical Company, Rochester, New York, has on its cover a photomicrograph of martensite. The contents of the magazine includes articles on "Diamond Turning," "An Example of Metallographic Research in the Manufacture of Scientific Instruments," and "Surveying Takes to the Air."

The Laboratory, magazine of the Fisher Scientific Company, Pittsburgh, Pennsylvania, and Montreal, Canada, features in its latest edition an article "William Kelly, the Forgotten Metallurgist," with an accompanying cover photograph of a Bessemer converter in operation at a Pittsburgh, Pennsylvania, steel mill. Mr. Kelly is said to have originated this converter process, bearing Bessemer's name.

Contributors to This Issue

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Thomas H. Osgood, after completing his undergraduate studies at the University of St. Andrews, Scotland, entered Rutherford's laboratory in Cambridge as a graduate student and received the Ph.D. degree there in 1927. He continued his research work as a Commonwealth Fund Fellow at the University of Chicago (M.S., 1927) and Mount Wilson Observatory. Before going to the University of Toledo in 1934 he held positions in the Universities of St. Andrews, Manchester and Pittsburgh.

T. H. Osgood

Julian H. Webb received his B.S. degree from Clemson College, South Carolina, in 1923, and his M.S. degree in 1925 and his Ph.D. degree in 1929 from the University of Wisconsin. From 1925 to 1929 Dr. Webb was assistant in the Physics Department at the University of Wisconsin, and from 1929 to 1931 was an Instructor in Physics at Williams College. He joined the Kodak Research Laboratories in 1931 and since has been working in the field of photographic theory.

R. Kingslake

J. Wallace Reddie took his B.S. degree in chemistry at Tufts College in 1927. He did control work in the Department of Research and Technology of the United Drug Company for the next eight years. During the past four years he has been devoting his time to research on the application of physical and chemical methods to pharmaceutical manufacturing.

J. W. Reddie

R. Kingslake was born in London, England, and attended the Optical Engineering Department at the Imperial College between 1921 and 1927. He spent a year with Grubb Parsons and Company, and a year with the International Standard Corporation in England, and was then appointed Assistant Professor of Optics at the University of Rochester. He joined the lens design staff of the Eastman Kodak Company in 1937.

T. R. Wilkins

David L. MacAdam received a B.S. at Lehigh University in 1932 and a Ph.D. at the Massachusetts Institute of Technology in 1936. He was a co-author of the *Handbook of Colorimetry*, and is a member of the Colorimetry Committee of the Optical Society of America. Since 1936 he has been with the Kodak Research Laboratories.

D. L. MacAdam

T. Russell Wilkins received his Ph.D. degree from Chicago in 1921. Since 1926 he has been Professor of Physics at Rochester. He organized, and for eight years was Acting-Director, of the Institute of Optics. His main research has been in the use of photographic emulsions in the study of radioactivity and cosmic rays, in connection with which he has been awarded the medal of the Royal Photographic Society for 1939.

John F. Kincaid has attended Central College, The George Washington University, and Princeton University, receiving his Ph.D. in Chemistry from Princeton in 1938. He is now Instructor in Chemistry at the University of Rochester. His research work has included experimental work on pure liquids and solutions, theoretical work on liquids and reaction rates, and, recently, problems of a physical organic nature.

D. Frisch

J. F. Kincaid

David Frisch comes from San Antonio, Texas. He is at present a senior at Princeton University, where he is majoring in physics.

Henry Eyring was born in Colonia Juarez, Mexico, in 1901. He received the B.S. degree in mining and the M.S. degree in metallurgy from the University of Arizona. In 1927 he received his Ph.D. degree from the University of California. He has served as Instructor at the University of Wisconsin, National Research Fellow in Berlin, and lecturer at the University of California. He is now Professor of Chemistry at Princeton University.

H. Eyring

Ronald L. McFarlan's picture and biography appeared on p. 580 of Vol. 9, No. 9, September, 1938.

C. H. Bachman's picture and biographical sketch will appear in the February issue.

Here and There

Rumford Medal Award

Award of the Rumford Medals to Professor George Russell Harrison, Professor of Physics and Director of the Research Laboratory of Experimental Physics at the Massachusetts Institute of Technology, was made October 11, 1939, by the American Academy of Arts and Sciences.

Count Rumford's gift of $5000 to the Academy in 1796 made possible the award of the Rumford Medals. The letter accompanying the gift specified that the proceeds therefrom should be "applied and given once every second year, as a premium, to the author of the most important discovery or useful improvement on Heat, or on Light; the preference always being given to such discoveries as shall, in the opinion of the Academy, tend most to promote the good of mankind."

Professor Harrison's contributions to the knowledge and technique of spectroscopy make him a worthy recipient of the honor of the Rumford Medals. In addition to his valuable research work, Professor Harrison has written a recent book, *Atoms in Action*. During the last seventeen years he has published thirty-five papers in his own name and eleven in collaboration with others.

Necrology

Professor Jonas Bernard Nathanson, Associate Professor of Physics at the Carnegie Institute of Technology, Pittsburgh, Pennsylvania, died November 25, 1939. Dr. Nathanson was born in Vilna, Lithuania, in 1889. He received his Ph.D. degree from the University of Illinois in 1916 and came as instructor in the same year to the Carnegie Institute of Technology. He had been Associate Professor there since 1930.

Bulletin of Mathematical Biophysics

The fourth issue of *The Bulletin of Mathematical Biophysics* has just appeared. This bulletin publishes quarterly contributions to the physico-mathematical foundations of biology. Inquiries concerning the bulletin should be addressed to its editor, Professor N. Rashevsky, University of Chicago, Chicago, Illinois.

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Duke University

In accordance with a resolution adopted by the Board of Trustees of Duke University, the Division of Engineering, which was administered as part of Trinity College, was reorganized into the College of Engineering of Duke University. W. H. Hall, Professor of Civil Engineering and Chairman of the Division of Engineering, has been appointed Dean of Engineering.

Contributed Original Research

Pressure and Temperature Effects on the Viscosity of Liquids*

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The free energy of activation for viscous flow is related to an entropy and energy of activation by the same equations as any equilibrium. This, for the theory of viscosity is perfectly general and independent of the mechanism. The rolling over each other of pairs of molecules lying in adjoining layers is the mechanism which appears to be the most probable, and the equations for this bimolecular flow process are developed here. At low pressures the heat of activation for viscous flow is about one-third the energy of vaporization, but as the pressure is raised, it increases rapidly because of the work term, PV/n'. Here P is the external pressure, V is molal volume and V/n' is the extra volume required before the flow process can take place. Calculations made for *n*-pentane, ether, benzene, iso-pentane, water, and mercury over as extended a temperature and pressure range as the data permit are found to agree satisfactorily with the experimental viscosity. The results are interpreted in terms of the liquid structure and the mechanism of viscous flow. The results of applying our theory to the liquids for which the necessary data is available show that the effect of pressure on viscosity can be calculated *a priori*, with thermodynamic data only, with reasonable success.

THE general equation for the rate of any process in which matter rearranges by surmounting a potential energy barrier has been proposed in the following form:[1-3]

$$k' = \kappa(F^*/F_n)(\bar{p}/m^*), \tag{1}$$

where F^* is the partition function for the activated complex per unit length normal to the potential barrier, $\bar{p}$ is the corresponding average momentum, and m^* is the reduced mass. F_n is the partition function for the normal state; κ is the transmission coefficient, the chance that a system having once crossed the potential barrier will react and not recross in the reverse direction. Eq. (1) states that the absolute rate of a reaction is the product of the number of molecules per unit length in phase space at the top of the barrier by the velocity at the top of the barrier, multiplied by an efficiency factor.

We assume that there is no "tunneling" under the barrier, and that the activated complex has nearly all the properties of an ordinary molecule except that instead of having only the three regular translational degrees of freedom, it has a fourth, along which it approaches the barrier, crosses it, and flies to pieces. We can now write (F^*/F_n) as $(F^\ddagger/F_n)(2\pi\mu^* kT)^{\frac{1}{2}}/h \exp(-\Delta E_0/kT)$ where $F^\ddagger$ is the partition function of the activated complex without the fourth degree of translational freedom per unit length represented by $(2\pi\mu^* kT)^{\frac{1}{2}}1/h$, and ΔE_0 is the energy of activation. The usual expression for the average velocity in the forward direction across the barrier is:

$$(\bar{p}/\mu^*) = (kT/2\pi m^*)^{\frac{1}{2}} \tag{2}$$

and Eq. (1) becomes

$$\begin{aligned} k' &= \kappa(F^\ddagger/F_n)(2\pi m^* kT)^{\frac{1}{2}}/h \\ &\quad \times \exp(-\Delta E_0/kT)(kT/2\pi m^*)^{\frac{1}{2}} \\ &= \kappa(F^\ddagger/F_n)kT/h \exp(-\Delta E_0/kT). \end{aligned} \tag{3}$$

Assuming $\kappa = 1$, this becomes

$$k' = (F^\ddagger/F_n)(kT/h) \exp(-\Delta E_0/kT).$$

* This paper was presented on December 29, 1938 at the Pittsburgh symposium of the Society of Rheology.

[1] H. Eyring, J. Chem. Phys. **3**, 107 (1935).

[2] Evans and Polanyi, Trans. Faraday Soc. **21**, 875 (1935).

[3] W. Wynne-Jones and H. Eyring, J. Chem. Phys. **3**, 492 (1935).

We now review[4-6] briefly the application of this general theory of reaction rates to liquids and treat certain aspects more explicitly. The most probable mechanism of liquid flow is the rolling past each other to new equilibrium positions of pairs of molecules in adjoining layers; the frequent occurrence of this basic process shifts the layers of molecules and constitutes flow. This process is illustrated in Fig. 4 of Hirschfelder, Stevenson and Eyring.[7] The configuration in which the molecules are halfway by each other, having broken part of their bonds and having also accumulated the necessary extra space, constitutes the activated complex. The activation energy required for the passing of the molecules is the energy of activation of viscous flow, $\Delta E_{vis}(\equiv\Delta E_0)$.

The distance measured along the velocity gradient between two neighboring pairs of molecules sliding past each other is taken as λ_1. The average distance between equilibrium positions in the direction of motion is taken as λ while the distance between neighboring molecules in this same direction is λ_2, which may or may not equal λ. λ_3 indicates the molecule-to-molecule distance normal to the direction of motion and to λ_2 and λ_1. By definition we have for the viscosity $\eta=f\lambda_1/\Delta v$. Here f is the force per square centimeter tending to displace one layer with respect to the other, and Δv is the difference in velocity of these two layers which are at a distance λ_1 apart. The force acting on a single molecule is $f\lambda_2\lambda_3$, and it acts to lessen the work of passing over the barrier through a distance $\lambda/2$, so that in the forward direction the height of the barrier is in effect lowered by the amount $f\lambda_2\lambda_3\lambda/2$, while in the backward direction it is raised by the same amount. The number of times that a molecule moves in the forward direction in a second may be written as the corresponding specific reaction rate:

$$k_f=(F^\ddagger/F_n)kT/h \times\exp\left[-(2\Delta E_0-f\lambda_2\lambda_3\lambda)/2kT\right]. \quad (4)$$

For the backward direction:

$$k_b=(F^\ddagger/F_n)kT/h \times\exp\left[-(2\Delta E_0+\lambda_2\lambda_3\lambda)/2kT\right]. \quad (5)$$

Hence:

$$\begin{aligned}\Delta v&=\lambda(k_f-k_b) \quad (6)\\ &=\lambda(F^\ddagger/F_n)hT/h \times\exp(-\Delta E_0/kT)\{\exp f\lambda_2\lambda_3/2kT) -\exp(-f\lambda_2\lambda_3\lambda/2kT)\}\\ &=\lambda(F^\ddagger/F_n)kT/h \times\exp(-\Delta E_0/kT)2\sinh(f\lambda_2\lambda_3\lambda/2kT)\end{aligned}$$

and

$$\eta=f\lambda_1/\Delta v=f\lambda_1[\lambda(F^\ddagger/F_n)kT/h \times\exp(-\Delta E_0/kT)2\sinh(f\lambda_2\lambda_3\lambda/2kT)]^{-1}. \quad (7)$$

Now for ordinary viscous flow $f\lambda_2\lambda_3\lambda\ll kT$, so that expanding the exponential and keeping the first power terms only we have after cancellation:

$$\begin{aligned}\eta&=\lambda_1kT[\lambda^2\lambda_2\lambda_3(F^\ddagger/F_n)kT/h \times\exp(-\Delta E_0/kT)]^{-1} \quad (8)\\ &=(\lambda_1h/\lambda^2\lambda_2\lambda_3)(F_n/F^\ddagger)\exp(\Delta E_0/kT).\end{aligned}$$

It is interesting to check the assumption $f\lambda_2\lambda_3\lambda\ll kT$. While Bridgman[8] does not give the exact data necessary to compute f, we can determine its order of magnitude. The annular space between the falling weight and the cylinder wall in his experiment was of the order of 10^{-2} cm. The weight fell at a velocity roughly of the order of 1 cm/sec. Viscosity is defined by the equation: $\eta=fd/\Delta v$ where d is the distance between the layers across which the velocity gradient Δv is measured.

$$f=\eta\Delta v/d\approx10^{-2}/10^{-2}=1\text{ dyne/cm.}^2$$

Since
$$\begin{aligned}\lambda_2\lambda_3\lambda&\approx V/N\\ f\lambda_2\lambda_3\lambda&\approx10^2/10^{23}=10^{-21}\\ T&\approx300^\circ K\\ k&\approx10^{-16}\text{ erg/deg./mole}\\ kT&\approx10^{-14}.\end{aligned}$$

So we are justified by a factor 10^{-7} in assuming $f\lambda_2\lambda_3\lambda\ll kT$. We develop somewhat more fully than has been done previously the form of the general expression

$$k'=(F^\ddagger/F_n)kT/h\exp(-\Delta E_0/kT)$$

for the particular case of a bimolecular process. By bimolecular we mean that molecules one and two in two contiguous layers move simultane-

[4] H. Eyring, J. Chem. Phys. **4**, 283 (1936).
[5] R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).
[6] H. M. Smallwood, J. App. Phys. **8**, 505 (1937).
[7] Hirschfelder, Stevenson and Eyring, J. Chem. Phys. **5**, 896 (1937).
[8] P. M. Bridgman, *The Physics of High Pressures* (Macmillan Co., 1931).

ously in such a way as to pass each other. If the coordinates of molecule one are $x_1y_1z_1$ and of two $x_2y_2z_2$, it is convenient to replace these with the three coordinates of the center of gravity of the pair

$$X=(m_1x_1+m_2x_2)/(m_1+m_2),$$
$$Y=(m_1y_1+m_2y_2)/(m_1+m_2),$$
$$Z=(m_1z_1+m_2z_2)/(m_1+m_2),$$

and the three components of the distance between the pair $x=x_2-x_1$, $y=y_2-y_1$, $z=z_2-z_1$. Now if the direction of flow is in the x direction, the activated state will correspond to $x=0$, and we can speak of x as the reaction coordinate. Using classical mechanics which is adequate for viscous flow in the cases with which we are here concerned, we obtain:

$$(F^{\ddagger}/F_n)(kT/h)=\delta q\int_0^{\infty}\exp(-p^2/2\mu^*kT)(p/\mu^*\delta q)dp\left[\int_{-\infty}^{+\infty}\exp(-p^2/2\mu^*kT)\int_0^{V_f^{\frac{1}{3}}}dx\right]^{-1}$$
$$=(kT/2\pi\mu^*)^{\frac{1}{2}}\cdot V_f^{-\frac{1}{3}}=(kT(m_1+m_2)/2\pi m_1m_2)^{\frac{1}{2}}V_f^{-\frac{1}{3}}. \quad (9)$$

The arbitrary length, δq, along the reaction path normal to the top of the potential barrier is seen to cancel out of the final result. Here we have assumed that $F^{\ddagger}$ and F_n cancel for all degrees of freedom except the reaction coordinate. The reduced mass in the x direction is $\mu^*=m_1m_2/(m_1+m_2)$. The limits 0 to $V_f^{\frac{1}{3}}$ for $x=x_1-x_2$ in the above integral follow from the fact that configurations of the normal state for which $x_1>x_2$, only, are to be considered.

This then gives us

$$F_n/F^{\ddagger}=(2\pi\mu^*kT)^{\frac{1}{2}}V_f^{\frac{1}{3}}/h, \quad (10)$$

where V_f is the free volume, defined as the total integral over that part of the potential energy which is due to thermal displacements of the center of gravity from its equilibrium position.

Combining Eqs. (8) and (10) we have

$$\eta=\lambda_1/\lambda^2\lambda_2\lambda_3(2\pi\mu^*kT)^{\frac{1}{2}}V_f^{\frac{1}{3}}\exp(\Delta E_{\text{visc}}/kT). \quad (11)$$

If λ is equal to λ_1,

$$\lambda_1/\lambda^2\lambda_2\lambda_3=N/V \quad (12)$$

and we have

$$\eta=(\pi RMT)^{\frac{1}{2}}/V(V_f^{\frac{1}{3}}/N^{\frac{1}{3}})\exp(\Delta E_{\text{visc}}/RT), \quad (13)$$

in which all units are now molar. Since we have assumed the process bimolecular, we have written $N\mu^*=(N(m_1m_2/m_1+m_2)=M/2$.

Kincaid and Eyring[9] develop the equation $V_f^{\frac{1}{3}}=(u_g/u_1)V_1^{\frac{1}{3}}$ where u_g is the velocity of sound in the gas and u_1 the velocity of sound in the liquid. Substituting we get

$$\eta=(\pi RMT)^{\frac{1}{2}}N^{-\frac{1}{3}}(u_g/u_1V_1^{\frac{1}{3}})\times\exp(\Delta E_{\text{visc}}/RT). \quad (14)$$

Both velocities may be evaluated by the hydrodynamic formula $u=(v/\beta_s)^{\frac{1}{2}}$ where v is the specific volume and β_s the adiabatic compressibility. This becomes $u_g=(\gamma RT/M)^{\frac{1}{2}}$ for an ideal gas, where γ is the ratio of specific heat at constant pressure to that at constant volume.

We must now evaluate ΔE_{visc}, the energy of activation for viscous flow. This energy is required to adjust the surroundings of a pair of molecules so that they can pass each other. At comparatively low pressures all that is needed is that some fraction of the bonds between two adjacent molecules and their neighbors be broken or stretched enough so that this pair can pass by each other. The energy of activation for viscous flow at low pressures turns out to be about $\frac{1}{4}$ the energy of vaporization. Our equation now becomes

$$\eta=(\pi RMT)^{\frac{1}{2}}N^{-\frac{1}{3}}(u_g/u_1V_1^{\frac{1}{3}})\times\exp(\Delta E_{\text{vap}}/nRT), \quad (15)$$

where n is a constant lying between 3 and 5 for normal liquids. The fraction of bonds broken is a function of the type of molecule and the structure of the liquid. For any normal liquid the fraction of bonds broken will not vary with the temperature, i.e., n is a constant. Hence the empirical rule, $\eta=A\exp(B/T)$.

This evaluation of the activation energy for viscous flow holds at comparatively low pressures only, for only then can we neglect the work of expansion against the external pressure necessary

[9] Kincaid and Eyring, J. Chem. Phys. **6**, 620 (1938).

to make the hole in which the molecules pass each other. At high pressures we must add on to $\Delta E_{vap}/nRT$ the term $P\Delta V/RT$ where P is the external pressure and ΔV the volume of the hole formed against it. ΔV will be some fraction V/n' of the molecular volume, giving

$$\eta = (\pi RMT)^{\frac{1}{2}} N^{-\frac{1}{3}} (u_g/u_l) V_l^{-\frac{2}{3}} \times \exp(\Delta E_{vap}/nRT + PV/n'RT). \quad (16)$$

n' will often vary over the experimental pressure range because as the liquid becomes compressed and the molecular volume decreases, a different fraction of the molecular volume is needed to give the same amount of space for the passing of molecules. Liquids such as water undergo structural changes under pressure that would naturally alter rapidly the free space available for molecular passage without making an additional hole, thus affecting n'.

Solids unlike liquids are not able to introduce a hole a fraction the size of a molecule without profoundly altering the crystal structure in the neighborhood of the molecules passing each other. This alteration in structure could take the form of a compression of neighboring molecules. In this case it can be estimated from the well-known thermodynamic expression for the free energy of compression. This way of obtaining the necessary cavity permitting viscous flow would be expected to be more extravagant of free energy than the method of over-all expansion possible in the comparatively structureless liquids. In fact in solids it may be cheaper from the free energy point of view to diffuse only where a molecule is omitted from the lattice than by distortion of a perfect lattice.

The procedure followed in the computations is to use the experimental viscosity, the energy of vaporization, the velocity of sound in both the liquid and the gas, and the other terms on the right-hand side of Eq. (15) to determine n, giving the proper temperature variation of viscosity. This is done over as wide a temperature range as the data warrant and at atmospheric pressure, employing the sound velocity data of Freyer, Hubbard and Andrews,[10] and other data from *Landolt-Bornstein Tabellen*. The values of n obtained in this way, given in Table I, are then used in Eq. (16) in order to obtain values of n' at a given temperature and different pressures. The viscosity and P-V-T data are those given by Bridgman.[8] By the use of the P-V-T data, the energies of vaporization were in all cases corrected to the particular pressure in question. A summary of the results for n' is given in Table II.

The values of n given in column three of Table I lie in a slightly different range than those of Ewell and Eyring[5] shown in column two because a different evaluation of the free volume has been used here. Column six of Table I shows that the value for n which gives the right temperature coefficient of viscosity also gives the absolute value to within better than an average factor of 2 for liquids other than those classed as "hydrogen-bonded."

TABLE I.

SUBSTANCE	n, E. AND E.	n (THIS PAPER)	n' (MEAN VALUE)	n'/n (THIS PAPER)	η(obs.) η (COMPUTED)
n-Pentane	3.5	4.4	7.8	1.8	1.1
Diethyl Ether		4.5	7.8	1.6	1.9
Benzene	2.6	3.3	5.5	1.7	0.6
Iso-Pentane		4.4	8	1.8	1.9
Mercury	20	11	23	2.1	2.8

TABLE II. *Values of n′ as computed from the data at various pressures.*

PRESSURE kg/cm²	n-PENTANE 30°C	DIETHYL ETHER 52.5°C	BENZENE 25°C	ISO-PENTANE 50°C	MERCURY 0°C	WATER 0°C
1,000	6.0		5.5	8		124
2,000	6.9	4.7			25.0	14
4,000	8.5	6.0			23.0	8.0
6,000	9.7	6.8			21.2	(5000)7.2
8,000	10.4	7.2				
10,000	10.8	7.6				
12,000		7.9				

The individual computations of n' are shown in Table II. The treatments possible for benzene and for iso-pentane warrant giving only one value for n'. It will be noted that n' for n-pentane, ether, and mercury does not vary greatly over the entire experimental pressure range, but that n' for water ranges from 124 at 1000 kg/cm² to 7.2 at 5000 kg/cm.² This variation is interpreted as follows: at low pressures water has an open, four-coordinated structure,[11]

[10] Freyer, Hubbard and Andrews, J. Am. Chem. Soc. **51**, 759 (1929).

[11] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 540 (1933).

and no extra volume is required for the activated complex for flow to form. As the pressure is increased, the open structure collapses, and at high pressures the activated complex needs as much extra space to form as is required by any other nonspherical molecule. It is probably incorrect to assume that n is constant for these liquids at one temperature and varying pressures, but the value of n' is not greatly affected by a considerable change in n. Table III illustrates

TABLE III. *Values of n' for water for different values of n at 0°C.*

P (kg/cm)	$n=2$	4	5.4
1,000		16.1	124
2,000	32	16	14
3,000	19	11	9.7
4,000	14	8.8	8.0
5,000	10.6	7.7	7.2

that the n' values computed for water using different n's converge to about the same limit at high pressures.

The fifth column of Table I gives the ratio of the mean value of n' over the pressure range to the value of n. The fact that this ratio is nearly constant and equal to 1.6–1.8 for the four nonmetallic liquids in the table is of some significance. It has been previously shown[4] that the energy required to form a hole in a liquid the size of a molecule is equal to the energy of vaporization. Although it might be reasonable to assume a linear relationship between the size of the hole formed and the energy required to form it, the fact that the ratio, n'/n is not unity, but 1.75 indicates that this is not the case. Taking the data for ether as an example, we find an n' of 7, indicating that a hole approximately 1/7 the size of the molecule is required for viscous flow. However, the activation energy is 2/9 times the energy of vaporization. We accordingly have the interesting physical result that there is an energy of dissociation of large holes into smaller ones, i.e., two holes, each 1/7 the size of a molecule cost considerably more energy than one hole 2/7 molecular size. In case of ether, seven holes, each 1/7 the size of a molecule would liberate energy equal to 14/9 the energy of vaporization, on being combined into a single cavity of molecular dimensions.

The ratio n'/n for mercury does not differ greatly from that for the nonmetallic liquids in the Table, but n and n' are themselves much greater. This has been previously explained[5, 12] as being due to movement of the metallic ions in viscous flow, rather than of the atoms. That the ratio of n' to n is again approximately two for a hole as small as 1/23 the size of the atom is an interesting fact.

Figure 1 shows plots of observed and computed viscosities as a function of pressure for ether, mercury, and n-pentane, with constant values of n and n' in Eq. (16). The results of the present work lead us to suggest that viscosities under pressure may be computed with reasonable accuracy by Eqs. (15) and (16) by using only thermodynamic data and viscosity measurements at atmospheric pressure. For normal, nonmetallic liquids n' for use in Eq. (16) is equal to 1.75 times the value of n from Eq. (15). For metallic liquids the factor (n'/n) may be somewhat higher but only one test case is available. Although it is impossible at present to *predict* the pressure effect on viscosity for liquids in which the molecules are bound by directional bonds

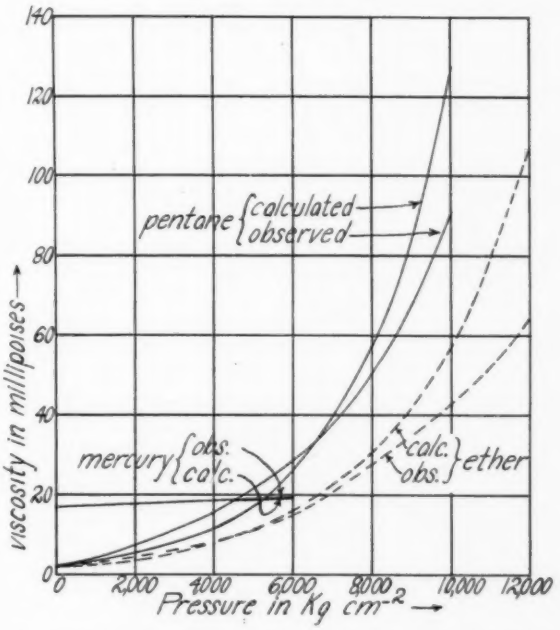

FIG. 1. Comparison of observed viscosities and those computed from Eq. (16). The values of n are 4.5, 12 and 4.4 of n' 8, 23 and 10 for ether, mercury and pentane, respectively.

[12] J. Kincaid and H. Eyring, J. Chem. Phys. **5**, 588 (1937).

TABLE IV. *Summary of data used in the computations.*

LIQUID	PRESSURE IN kg/cm²	$(\partial E/\partial V)T$ IN kg/cm²	E_{vap} kg/cm	FREE VOLUME IN cc/mole	OBSERVED VISCOSITY IN MILLIPOISES
n-Pentane at 30°C	1	1,640	238,800	1.21	2.20
	1,000	2,420	269,600	0.32	4.54
	2,000	2,310	283,050	.151	7.35
	3,000	2,110	291,010	.097	
	4,000	1,480	296,950	.068	15.5
	5,000	150	298,630	.053	
	6,000	−620	298,120	.044	28.5
	7,000	−1,240	296,520	.036	
	8,000	−1,090	294,850	.029	50.4
	9,000	−910	293,650	.023	
	10,000	−1,150	292,650	.020	90.7
Diethyl Ether at 52.5°C	1	2,190	227,500	1.52	1.83
	1,000				
	2,000	2,400	272,800	.128	5.46
	4,000	1,860	286,200	.071	10.50
	6,000	970	291,800	.048	17.58
	8,000	120	293,200	.034	27.75
	10,000	1,370	291,900	.028	42.69
	12,000	−2,050*	290,400	.023	64.24
Water at 0°C	1	−162	435,500	0.439	17.92
	1,000	+518	435,540	.292	16.50
	2,000	775	436,000	.204	17.15
	3,000	845	436,730	.149	18.35
	4,000	673	437,800	.114	19.91
	5,000	−112	438,900	.096	21.83
Mercury at 0°C	1	12,675	599,800	0.0119	
	2,000	12,186	601,100	.0114	
	4,000	12,355	602,100	.0109	
	6,000	12,928	602,900	.0105	

* At 11,000.

(e.g., water and alcohols), the method of computation employed here yields interesting information about the structure and the mechanism of viscous flow in such liquids.

In our calculation of viscosities we have treated the flow of individual molecules only and have neglected the fact that aggregates of molecules can flow as units also. More precisely to the calculated fluidity for the single mechanism we should add the fluidity due to the double, triple and higher multiple molecule mechanisms. That our approximation ordinarily neglects factors considerably smaller than two in the fluidity may be seen by comparing the theoretical or experimental fluidity of molecules with values for molecules twice as large but otherwise similar. This aspect of the subject will be developed in detail at a later time.

APPENDIX

Since the data used in making the computations are of some interest for their own sake, they are assembled in Table IV. The data for benzene and for iso-pentane have not been done in enough detail and are over too short a pressure range to justify their inclusion in this Table. The free volumes have been computed from sound velocities, and the thermodynamic data are from the data given by Bridgman.[8]

An X-Ray Study of Acetylsalicylic Acid When Incorporated in Certain Sugars

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INTRODUCTION

CONFLICTING claims have recently been advanced regarding the possibility of incorporating acetylsalicylic acid—aspirin—into certain sugar bases as a solid solution. The original claims made regarding the existence of such a solid solution[1] have been subsequently denied[2] as a result of certain x-ray experiments. In these latter experiments only x-ray diffraction patterns consisting of a series of sharp lines—characteristic of a mixture of powdered crystalline fragments—are reported. Unpublished preliminary x-ray studies of this problem made in the summer of 1935 yielded a diffraction pattern for the sugar bases consisting of a single, broad diffuse ring—characteristic of an amorphous or glass-like material. Since the types of x-ray patterns obtained differ so sharply it has seemed worth while to examine once more the whole problem from an x-ray point of view.

PREPARATION OF SAMPLES

Sucrose and glucose were mixed with sufficient additional water to assure a complete solution of

[1] E. C. Merrill, Chem. Abs. **31**, 5949 (1937).
[2] S. S. Sidhu, J. App. Phys. **9**, 546 (1938).

TABLE I.

Diffraction Pattern Number	Percent Aspirin	Aspirin Incorporation Temperature	Observation
1	0.0	21°C	Diffuse pattern.
2	0.7	21	Diffuse pattern, aspirin lines weak but definitely present.
3	1.0	21	Diffuse pattern, aspirin lines present
4	2.0	21	" " " " "
5	5.0	21	" " " " "
6	100.0	—	Diffuse pattern missing.
7	0.7	102	Diffuse pattern, aspirin lines just show.
8	0.7	121	Diffuse pattern altered, rings of smaller diameter, no aspirin lines.
9	1.28	121	Diffuse pattern altered, rings of smaller diameter, no aspirin lines.

the sugars, and the resulting syrup was heated to 143°C—a temperature sufficiently high to remove essentially all of the water. Upon reaching this temperature the sugar mass was cooled to the temperature at which the aspirin was incorporated—121°C. The sugar mass was held at this temperature until all visible traces of the added aspirin disappeared. For aspirin concentrations of 2 percent or less, it was found necessary to keep the sugar mass at the incorporation temperature for about twenty minutes. When cooled, the resulting sugar-aspirin mass appeared glassy and transparent. All ingredients used in this investigation were of U. S. Pharmacopoeial grade.

Experimental Procedure

The sugar-aspirin masses were stored in closed, desiccated containers until ready for use. Samples were powdered, loaded into thin-walled Lindemann glass tubes about one-half millimeter in diameter and the glass sealed. Powdering, loading and sealing were done in an air-conditioned room whose humidity was maintained constant at 20 percent relative humidity. X-ray patterns were taken with the samples still in the sealed tubes so that moisture from the air could not get at the samples. The tubes were placed at the center of a Debye-Scherrer powder camera and exposed to filtered copper radiation for about eight hours. The radius of the camera was 4.74 cm and the wave-length of the x-rays 1.539A.

The sugar-aspirin masses were also chemically analyzed for the percentage of recoverable acetylsalicylic acid. The double titration method officially recommended by the A.O.A.C.[3] was used. Except for the mechanical aspirin-sugar base mixes, the acetylsalicylic acid percentages given in the table below are those determined by the official A.O.A.C. method.

[3] *Methods of Analysis*, A.O.A.C. (1935), fourth edition, p. 551.

Results

There are, in general, three types of diffraction patterns to be expected when taken under the above conditions. (a) A series of sharp lines such as was obtained from the sample of pure aspirin. This pattern is indicative of a sample which is largely crystalline. (b) A pattern of broad, diffuse rings such as was obtained from the pure candy base. This pattern is characteristic of a sample which is largely amorphous. (c) A superposition of the first two patterns, an example of which is the mechanical mix of 5 percent aspirin. This type of pattern is typical of a sample consisting of a mixture of crystalline and amorphous material. By observing the relative intensity of the line pattern as compared with the diffuse pattern, it is possible to tell what the relative amounts of crystalline and diffuse materials are. The results obtained are summarized in Table I.

Diffraction patterns 2–5 inclusive are due to mechanical mixtures of aspirin and pure candy base, made by grinding carefully weighed amounts of the two ingredients together with a mortar and pestle. The sharp diffraction lines due to crystalline aspirin present in a concentration of 0.7 percent are definitely detectable, but are weak.

Diffraction pattern No. 7 was taken with a sample in which the aspirin was incorporated into the candy base at too low a temperature to enable the aspirin to go completely into solution within a twenty-minute limit. The sharp aspirin

diffraction lines perhaps appear to be a little weaker than the lines in pattern No. 2.

Diffraction patterns No. 8 and No. 9 show no trace whatever of the sharp powder diffraction lines of aspirin, although the A.O.A.C. method of analysis reveals concentrations of aspirin present which, if crystalline, would produce readily detectable diffraction lines.

In all of the patterns except the one of pure aspirin the diffuse pattern of the amorphous candy base was present. This diffuse pattern was essentially the same for all the samples except for the two where the aspirin was added at 121°C, in which case the diffuse rings on the pattern were of somewhat smaller diameter. A sample of pure candy base which underwent the same temperature treatment as samples No. 8 and No. 9 gave essentially the same diffuse pattern as that found for all amorphous sugar base samples except No. 8 and No. 9.

Conclusions

The lowest concentration of aspirin tested was 0.7 percent. Below this concentration, the x-ray method is not sufficiently sensitive to decide whether or not there is crystalline aspirin present. Neither does it say whether or not small fractions of acetylsalicylic acid, at any of the concentrations studied, are in any other than the crystalline state.

In the samples where aspirin was added at 121°C, there is no x-ray evidence of crystalline aspirin. This means that there is less than 0.7 percent crystalline aspirin in the sample. In the case of sample No. 9, with a concentration of 1.28 percent aspirin, there must be at least 1.28−0.7 or 0.58 percent aspirin in the amorphous state, or in other words in solid solution. That the aspirin is still present as aspirin is demonstrated by the fact that the concentrations of 1.28 percent and 0.7 percent were recoverable by the official A.O.A.C. method.

The change in the diffuse pattern is another indication that the amorphous material in the sample is not entirely the original candy base. It is possible that the atomic distribution of the candy base has been altered by the aspirin. On the other hand, the aspirin—which is not crystalline—is present in an amorphous state, thus giving rise to two superposed diffused patterns, the resultant of which may be somewhat different from the diffuse pattern of the original candy base.

In conclusion, it can be said that a definite change from the crystalline to the amorphous state has been demonstrated for at least some of the aspirin incorporated into the candy base at 121°C. Since it is reasonable to suppose that the amorphous aspirin is homogeneously dispersed throughout the candy base, it consequently follows that the amorphous acetylsalicylic acid is in solid solution in the amorphous sugar mass.

The authors wish to express their appreciation to Mr. J. M. Anderson of the United Drug Company for making the analyses for recoverable aspirin, and to Professor B. E. Warren of the Massachusetts Institute of Technology and his assistants for taking the x-ray diffraction photographs described in this paper.

Ring Focusing of Negative Ions in a Cathode-Ray Beam

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(Received July 7, 1939)

An explanation is offered for the ring structure and some of the other configurational details associated with negative ion spots on fluorescent screens. Negative ion liberation by positive ion bombardment and the effect of the magnetic deflecting field on the positive ion paths are believed responsible for the apparent selective focusing of negative ions.

IN a previous publication[1] concerning the negative ions present in electrostatically focused electron beams, circles were obtained in certain instances either in addition to or in place of the focused spots ordinarily obtained. One of the figures of that paper is reproduced here, Fig. 1. Each of the radial rows of circles constitutes a negative ion spectrum obtained by magnetic deflection of a central beam associated with the electron beam. These were obtained with a typical electrostatically focused electron gun having in this case a tungsten filament.

It will be noticed that in every case a rather intense ring of constant diameter is obtained. These rings have different widths and degrees of shading. Some of them have focused center spots and some also have a focused spot in the ring itself, this always occurring in the radially outermost section of the ring. No explanation of these phenomena was offered at the time of publication.

The details of the gun structure and operating fields were not given and recently in a description of a new process for formation of negative ions by negative ion bombardment of surfaces, Sloane and Cathcart[2] attributed the above-mentioned rings as possibly due to the bombardment of a gun aperture by negative ions from the filament.

Although the assumption that the source was a bombarded gun aperture was correct, it is believed that the bombarding particles were not negative ions but positive ions. Tests with marked apertures indicate that the grid is the source of these rings and as it was at all times operated below cathode potential negative ions would pass it by in favor of the first anode which was at a relatively high positive potential. Furthermore, visual examination of similar guns after long periods of operation shows definite indications of intense positive ion bombardment of the grid aperture on the side away from the cathode. Formation of negative ions by positive ion bombardment has already been well demonstrated,[3-6] and it is believed that this action is responsible for the rings under discussion.

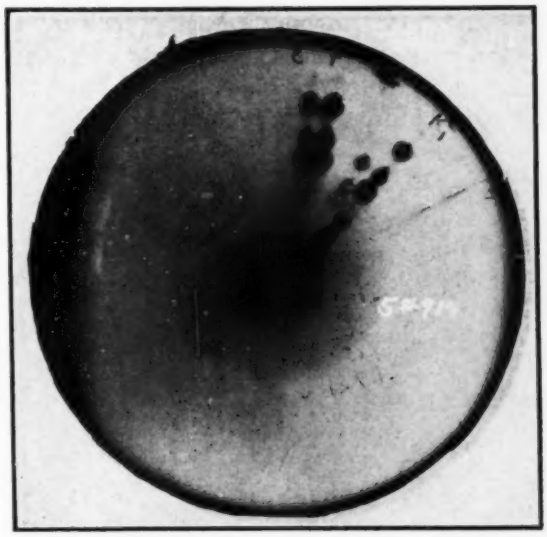


FIG. 1. Photograph of C.R. tube with screen fluorescing weakly and showing a series of negative ion "ring" spectra.

* Part of this work was carried on while the author was associated with Hygrade Sylvania Corporation.

[1] C. H. Bachman and C. W. Carnahan, "Negative ion components in the cathode-ray beam," Proc. I.R.E. **26**, 529–539 (1938).

[2] R. H. Sloane and I. Cathcart, "Formation of negative ions by negative-ion bombardment of surfaces: a new process," Nature **143**, 474 (1939).

[3] F. L. Arnot, "A new process of negative ion formation —II," Proc. Roy. Soc. **158A**, 137–156 (1937).

[4] F. L. Arnot and C. Beckett, "Formation of negative ions at surfaces," Nature **141**, 1011–1012 (1938).

[5] R. H. Sloane and R. Press, "Formation of negative ions at surfaces," Nature **141**, 872 (1938).

[6] R. A. Smith, "Formation of negative ions at metal surfaces," Proc. Roy. Soc. **168A**, 19–42 (1938).

The mechanism responsible for the particular structures of rings and spots obtained may be understood with the help of the accompanying diagrams. The general type of gun structure used with typical potentials is shown in Fig. 2 and the other diagrams are exaggerated views of the grid-cathode region and the paths of the charged particles involved.

Positive ions formed in the bulb space will be drawn toward the screen. Those formed in the neck of the tube in the fields due to gun potentials will be drawn in the direction of negative field, that is, toward the cathode. The first anode will intercept many of these. Some traveling near the axis, however, will act as a focused beam and pass straight through toward the cathode. From this beam some will be drawn out and bombard the grid which is more negative than the cathode although most of the focused ions will proceed directly to the cathode. This is shown in Fig. 3.

beam but will proceed directly to the grid. Traveling through a much lower voltage the center column of these ions will practically all be swept out to the grid. The innermost of the three intense rings of a spectrum of Fig. 1 shows this type of mechanism specifically, the greater diameter of this ring resulting from the lower voltage positive ions being swept farther off axis.

In Fig. 4 are shown the paths of the negative ions resulting from this bombardment of grid and cathode. Those from the cathode focus like electrons and are contained in the bundle designated (*C*). Because of the circular aperture, the ions from the grid, however, form the hollow sheath (*RR*) and give rise to a focused ring. Examination of the various rings indicates that though fundamentally associated with the grid aperture diameter the intensity distributions through cross sections of the rings are widely different. Also, the appearance of spots either in the center or in the ring section is not consistent from ring to ring in a given spectrum. It seems likely that positive ion bombardment of the circular edge or "corner" of the grid aperture should be particularly productive of negative ions. This accounts for the sharp maximum

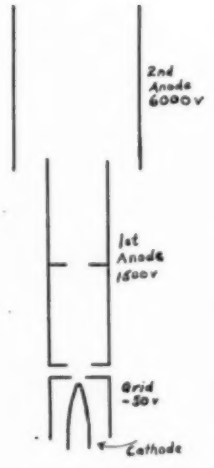


FIG. 2. Arrangement of typical gun.

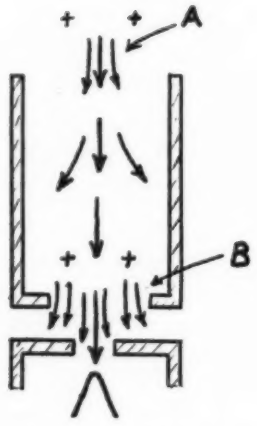


FIG. 3. Normal positive ion bombardment of grid-cathode region.

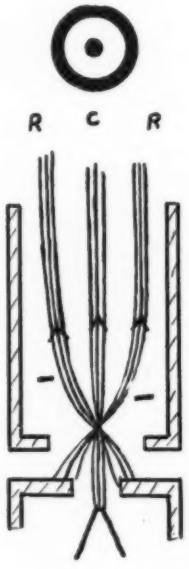


FIG. 4. Negative ions resulting from bombarding shown in Fig. 3.

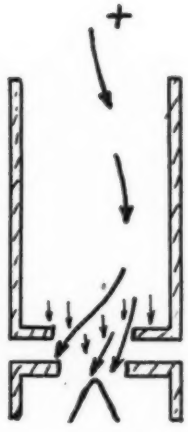


FIG. 5. Effect of ion deflecting field on positive ion beam.

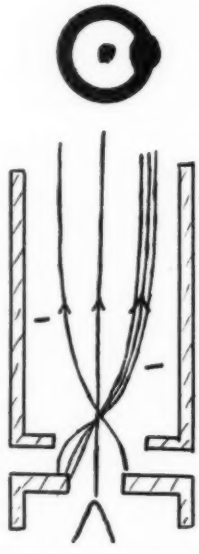


FIG. 6. "Edge spot" resulting from positive ion bombardment shown in Fig. 5.

ring. The broad diffuse portion of the ring outside this maximum can be attributed to negative ion emission resulting from bombardment of the anode side of the grid disk, chiefly by the positive ions formed in the grid-first anode field. The weaker inner portion of the ring arises from positive ions striking the inner wall of the grid aperture.

The center spots evident in nearly all the rings are, of course, due to negative ions originating near the cathode. The spots in the radially outermost parts of several of the rings are due to the interaction of the strong ion deflecting magnetic field with the electrostatic focusing fields. The beam of focused positive ions ordinarily passing down the tube axis to the cathode is deflected off axis by the magnetic field. Part of it then passes through crossover causing bombardment of a portion of the grid as well as the cathode (see Fig. 5). The result is an increased negative ion yield in this localized area so that the spot in the ring appears (see Fig. 6). The short arrows indicate the ions formed in the first anode and which contribute to the usual ring. In the case of a ring not having this "edge spot" it means that this particular positive ion was not present in the focused beam formed in the first anode—second anode region. No correction for measurements of ions from the cathode and grid need be made because their potential difference is negligible compared to the second anode potential which finally acts upon the ions.

It is significant that with an oxide-coated cathode focused spots are always obtained, with rings appearing only occasionally and then only around particular spots. This indicates that most of the positive ions are formed in the first anode —second anode region and are highly focused. For this reason, it is nearly impossible to distinguish between the possible ion forming mechanisms present at the cathode, those including positive ion bombardment, ionization of neutral particles or positive ions by acquisition of an electron or electrons in the space charge region or a similar action in the actual cathode structure resulting from the electrolytic phenomena present during cathode operation.

Examination of oxide-coated cathodes which have been subject to bombardment by positive ions indicates that the focusing is very efficient and pitting occurs in a very small spot on the cathode. The negative ion spots due to components of mass = 26 and mass = 35 and 37 have been found to be very well focused whereas components mass = 12, 16, 32 and some others are definitely diffuse. In general this has also been observed by Broadway and Pearce.[7] It would seem that the sharply focused spots are due to negative ions arising close to the axis of the gun as a result of positive ion bombardment. The diffuse spots, however, must come from a much larger area of the cathode since the diffuse range is much greater than would be given by the voltage distribution of excess energy. This is what might be expected of oxygen and carbon evolving from a thermionic cathode and picking up electrons by one of the mechanisms listed above.

In the tungsten filament tube rings were always obtained and several had no center spot. In this case, positive ion bombardment of the apertures is the predominant method of negative ion formation and it appears that most of the positive ions are formed in the first anode. In the cases where neither a center spot nor an "edge spot" appears, this must be entirely so.

The material presented here has been chiefly an explanation of phenomena presented in a previous paper.[1] It might be well to mention also that in the earlier publication it was stated that no negative ion component due to hydrogen had been found. Since then, a spot due to atomic hydrogen has been obtained in especially prepared tubes. It is also of interest to note that a negative ion spectrum has been obtained of sufficient intensity to cause fluorescence of the screen due to negative ion bombardment. This tube retained a vacuum sufficient to give normal electrical operation.

[7] L. F. Broadway and A. F. Pearce, "Emission of negative ions from oxide cathodes," Proc. Phys. Soc. **51**, 335–348 (1939).

Innovations in Instruments

Plastics Awards

Awards in the Fourth Annual Modern Plastics Competition, conducted by Modern Plastics Magazine, were formally made at a presentation dinner at the Waldorf Astoria on November 14.

Among the instruments receiving major awards were the "Balar" field glasses, produced by Bausch and Lomb Optical Company of Rochester, New York. These small field glasses, of Bakelite molding material, supplied by Bakelite Corporation of New York City, are specially designed to be carried in the pocket or purse, thus making them an excellent glass for sports purposes. The rectangular shape permits a wide field of vision.

Another award went to an invisible contact lens designed by William Feinbloom, New York City, for Optical Research, Inc. The lens is intended to overcome visual difficulties caused by kerotoconus and scarred corneas and to replace ordinary spectacles wherever desirable.

The Orsatomat, a crystal clear automatic gas analyzer which enables the researcher to watch the process through its transparent walls, received Honorable Mention in the Plastics Competition. This instrument is a product of The Hays Corporation, Michigan City, Indiana.

New Instruments

The Leeds and Northrup Company of Philadelphia announce the presentation of the following new products at the 1939 Chemical Show in New York City recently:

An SO_2 control which may be operated pneumatically or electrically and which introduces an entirely new combination of filter and gas analysis cell.

An optical pyrometer whose advantages over the older models include the ease with which it can be sighted and the decreased weight of the instrument.

Low Range Ohmmeter

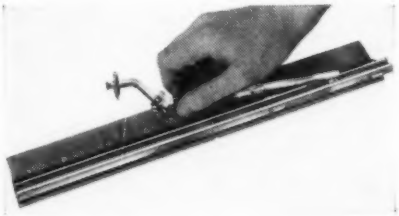
The Hickok ultra-low range ohmmeter, Model 4975-S, gives highly accurate measurements at low values of resistance on two ranges, —0–6 ohms and 6–600 ohms. The two ranges are nonoverlapping, thus permitting battery adjustment at the logarithmic center of the accurate section of the instrument's scale. Over-all accuracy is approximately plus or minus one degree of scale deflection, the scale being 100 degrees. This ohmmeter is made by The Hickok Electrical Instrument Company, 10514 Dupont Avenue, Cleveland, Ohio.

Spencer Opens New Plant

The opening of the new, additional Spencer Lens Company plant in Cheektowaga, New York, was marked by an "Open House" October 26 for employees, local business and professional men, and editors of business publications. Over 2000 people attended this expansion celebration, opening a plant to be devoted to the manufacture of mechanical parts. In the ninety-two years since Charles A. Spencer, first American microscope maker, engaged upon commercial production, Spencer instruments have come into use in the fields of metal, glass, ceramics, textile, paper, food and drug, paint and varnish manufacture; in crime detection devices; and in optical instruments for the American Optical Society.

Lettering Set

The Eugene Dietzgen Company, 2425 Sheffield Avenue, Chicago, Illinois, manufacturers of drafting and surveying supplies, made recent announcement of a new lettering set.



The Edco "Spee-dee" lettering set produces eight different types of lettering with one single guide. This is made possible by adjustment of setting of the tracer and the pen arm. Letters are formed in one continuous movement without shifting the guide, which has upper and lower case letters, numerals and characters.

New Waxes

The Glyco Products Company, Inc., 148 Lafayette Street, New York City, announces the following new products:

Acrawax has a melting point of 95–97°C. It is soluble, hot, in toluol, naphtha, turpentine, alcohol, mineral spirits and other hydrocarbon solvents. Solutions of Acrawax in these materials give clear, transparent gels on cooling. Acrawax is insoluble in water.

Ozowax has a melting point of 76–85°C. It is also soluble, hot, in the usual hydrocarbon solvents and solutions of the same produce clear, transparent gels on cooling.

Nipocer has a melting point of 46–49°C. It is soluble, hot, in toluol, naphtha, turpentine, etc. Nipocer emulsifies readily with the usual emulsifying agents, giving stable, smooth emulsions.

Samples, prices and further information can be obtained from the manufacturers.